A STUDY OF THE EXCITON THEORY IN MOLECULAR CRYSTALS

by

Chao N. Perng

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Peng Chao-Nan.

ABSTRACT

The exciton theory of pure molecular crystals is reviewed with special emphasis on the comparison between the treatment by perturbation methods and by the approximate second quantization method. The difference is discussed in terms of unitary equivalence, ground-state energy and the Heitler-London approximation. A numerical comparison on the 2500 Å band system of crystalline anthracene and on hypothetical bands with various combination of the transition moment, band position and dipole - dipole interaction sum is also made.

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TABLE OF CONTENTS

CHAPTER 1

Introduction -- Molecular Crystal Spectre

Many typical molecular crystals are formed from aromatic hydrocarbons such as naphthalene and anthracene. In these organic solids, the molecules are bound together by van der Waals forces. The forces are weak but there is an effect on the optically excited states and electronic spectra. Consequently, a comparison of the vapor and crystal absorption spectra shows that, although both spectra have the same characteristics, some significant features are found in the crystal spectra such as a multiplicity of crystal bands and the intensity differences for differently polarized radiation. The multiplicity does not exceed the number of molecules in the unit cell, and the energy intervals within the multiplet are called the Davydov (factor-group) splittings. The ratio of the intensity observed along two perpendicular directions in a crystal face is called the polarisation ratio.

Interpretation of these measured and calculated Davydov splitting and polarisation ratio is useful in two ways: firstly, it is known that while spectra of free molecules can yield the position of energy levels of the excited states relative to the ground state (transition frequency), and the probability of a transition from ground to an excited state (absorption intensity), they do not easily give the symmetry assignment of the energy levels. This observation is facilitated if the molecules are oriented. This condition is satisfied in molecular crystals so that interpretation of the molecular crystal spectra can supply the information about the symmetry assignment. Secondly, as is well known, there are mainly

two approximations used in dealing with solid-state problems. One is the Bloch approximation in which electrons are treated as freely moving but perturbed by a periodic potentials of positive charges. This approximation is used in the theory of metals. In the other approximation, electrons are assumed to be tightly bound to the molecule in the crystal and the interaction between molecules is treated as small perturbation. This is known as the weak-coupling model and is appropriate to the case of molecular crystals. Thus, the study of molecular crystal is useful in that from its results an increased understanding of tight-binding approximation can be obtained.

The modern theory of molecular crystal has been developed by Frenkel, Davydov, Craig and many other researchers. This theory can account, even within the framework of a rigid lattice, for the Davydov splitting and the polarisation ratio of the crystal spectra. Recently, there has been an increased interest in second quantization techniques. It is the purpose of this thesis to deal with the development of this new method in its application to the pure molecular crystals and to compare it with the conventional treatment using Frenkel-Davydov-Craig theory.

CHAPTER 2

Theory of Molecular Crystal in Coordinate Representation

2.1 Excitons

The exciton theory presented here is derived principally from Davydov,[4] Craig,[1,2] Craig and Walmsley.[3] The crystals being considered are restricted to those in which the molecules are crystallographically equivalent. Let h denote the number of molecules in the unit cell, N the number of unit cells in the whole crystal; M (=h.N) is then the total of crystallographically equivalent molecules in the molecular crystal. The ground state wave function of the crystal is given as a product of free molecular ground state wave function:

$$\underline{\psi}^{G} = \phi^{G}_{11} \ldots\ldots \phi^{G}_{ip} \ldots\ldots \phi^{G}_{hN} \qquad (2\text{-}1)$$

where ip denotes the i-th molecule in the p-th unit cell. Electron exchange between molecules is neglected and the basis functions for the crystal at different sites are assumed to be orthogonal:

$$\phi^{G}_{ip} \quad \phi^{G}_{jq} = \delta_{ij} \quad \delta_{pq} \qquad (2\text{-}2)$$

The molecular crystal is initially treated as a system of non-interacting oriented molecules (oriented gas model). The interaction between molecules is then applied to the crystal as a perturbation within the weak-coupling limit (1st order approximation). The pure crystal lattice is assumed as rigidly fixed so that the coupling between electronic transitions and molecular vibrations is ignored. The hamiltonian for the system is,

$$H = \sum_{ip} H_{ip} + \tfrac{1}{2} \sum_{ip \neq jq} V_{ip,jq} \qquad (2\text{-}3)$$

where H_{ip} is the hamiltonian for the isolated, p-th molecule and $V_{ip,jq}$ is the interaction potential energy between molecules. In the first order treatment, the ground state energy can be obtained as,

$$E_G = Mw^r + \tfrac{1}{2} \sum_{ip,jq} < \phi^G_{ip}\, \phi^G_{jq} | V_{ip,jq} | \phi^G_{ip}\, \phi^G_{jq} > \qquad (2\text{-}4)$$

w^r is the free molecular ground state energy.

When the molecule at the ip-th site is initially excited to its r-th excited state, all others are assumed to be in the ground state. Without any interaction, the excitation is localized and the wave function may be expressed as,

$$\Phi^r_{ip} = \phi^r_{ip} \prod'_{jq} \phi^G_{jq} \qquad (2\text{-}5)$$

the prime indicates that jq runs over all sites except for jq = ip. Due to the presence of intermolecular interaction, the excitation can migrate rapidly through the crystal lattice and the excitation is delocalized. This chargeless, collective excitation distributed throughout the entire crystal had been described by Frenkel as an 'exciton'. The exciton wave function is represented as a linear combination of localized wave funtions,

$$\psi^r_i = \sqrt{\frac{1}{N}} \sum_p C^r_{ip}\, \Phi^r_{ip} \qquad (2\text{-}6)$$

There would be h basis functions, i.e. $\psi^r_1 \quad \psi^r_{2,..} \quad \psi^r_h$, corresponding to h sets of translationally equivalent molecules. The crystal function can be defined as linear combination of these basis functions,

$$\psi = \sqrt{\frac{1}{h}} \sum_i^h B^r_i\, \psi^r_i \qquad (2\text{-}7)$$

The coefficients C^r_{ip} and B^r_i are not yet determined.

2.2. Group-theoretical Consideration

Group theoretical considerations become useful at this stage to determine the coefficients, C^r_{ip} and B^r_i. The crystal hamiltonian of (2-3) is invariant to the space group operations. The crystal wave functions can thus be generated according to the irreducible representations of the crystal space group. Since only the bulk (internal) properties are of interest, periodic boundary conditions can be introduced so that the crystal space group always possesses the group of primitive translation operations as an invariant subgroup with

$$C^r_{ip} = \exp (i \underline{K}. \underline{R}_{ip}) \qquad (2\text{-}8)$$

while $\underline{R} = n_1 \underline{r}_1 + n_2\underline{r}_2 + n_3\underline{r}_3$, $n_1n_2n_3$ are the components of the lattice vector $\underline{R}$ in the lattice vector basis $\underline{r}_1\underline{r}_2\underline{r}_3$ and $\underline{K} = k_1\underline{b}_1 + k_2\underline{b}_2 + k_3\underline{b}_{3j}$ $k_1k_2k_3$ are regarded as the components of a vector $\underline{K}$ with respect to the 'reciprocal' basis set $\underline{b}_1\underline{b}_2\underline{b}_3$ defined by

$$\underline{r}_i . \underline{b}_j = \delta_{ij} \qquad (2\text{-}9)$$

It can be seen that the vectors $\underline{b}_1\underline{b}_2\underline{b}_3$ also define a parallelepiped described as the unit cell of lattice in the reciprocal space. The values of k_i (i = 1, 2 or 3) can be chosen as lying in the range $-\pi \leq k_i < \pi$. The polyhedron enclosed is usually called the 'first' or 'reduced' Brillouin zone.

Substituting (2-8) into (2-6), the functions formed are known as Bloch functions:

$$\psi^r(\underline{K}) = \sqrt{\frac{1}{N}} \sum_{ip} \exp (i\underline{K}_r . \underline{R}_{ip}) \; \phi^r_{ip} \qquad (2\text{-}10)$$

In general, the space group contains more than primitive translation symmetry. Proper and improper rotations as well as nonprimitive translations such as screw rotations or glide reflections may be

present. In this case, the space group can be broken into the primitive translational subgroup (T) and all its nonequivalent cosets (A_1, A_2 ..) as:

$$\text{Space group} = T + T A_1 + T A_2 + \ldots\ldots$$

$$= (E|t_n)\ [(E|t_n) + (\alpha_1|\tau_1+t_n) + ..\ ] \qquad (2\text{-}10a)$$

E denotes the identity; α_1 denotes the rotational part, t_n denotes the primitive translational part (n = 0,1,2,..N-1) and τ the nonprimitive translational part of symmetry operations. $(E|t_n)$ is the primitive translation subgroup; $[(E|t_n) + (\tau_1|\alpha_1 + t_n) + (\tau_2|\alpha_2 + t_n) + \ldots]$, its cosets. These cosets form the factor group. It contains many symmetry elements and every element contains many symmetry operations due to the variable n. However, if only one unit cell is concerned, all the primitive translational parts of these symmetry operations are zero. Every element in this factor group contains one operation only and this group:

$$[(E|0) + (\alpha_1|\tau_1) + (\alpha_2|\tau_2) + \ldots\ldots]$$

is called the unit cell group. The factor group as well as the unit cell group is important for the analysis of crystal spectra, since the allowed wave functions must transform as irreducible representations of the factor (or unit cell) group.

Also there is a site group whose operations have the form $\{\alpha|0\}$. It can be formed by those unit cell group operations in which the nonprimitive translational parts are zero, so the site group is a subgroup of the unit cell group. Each operation in this group will transform each site on to itself. If each site is occupied by a molecule, the site group operations will also leave the molecule invariant, so the site group is also a subgroup of molecular point group. By setting up a correlation relationship among the factor (or unit cell) group, the site group and the molecular point group,

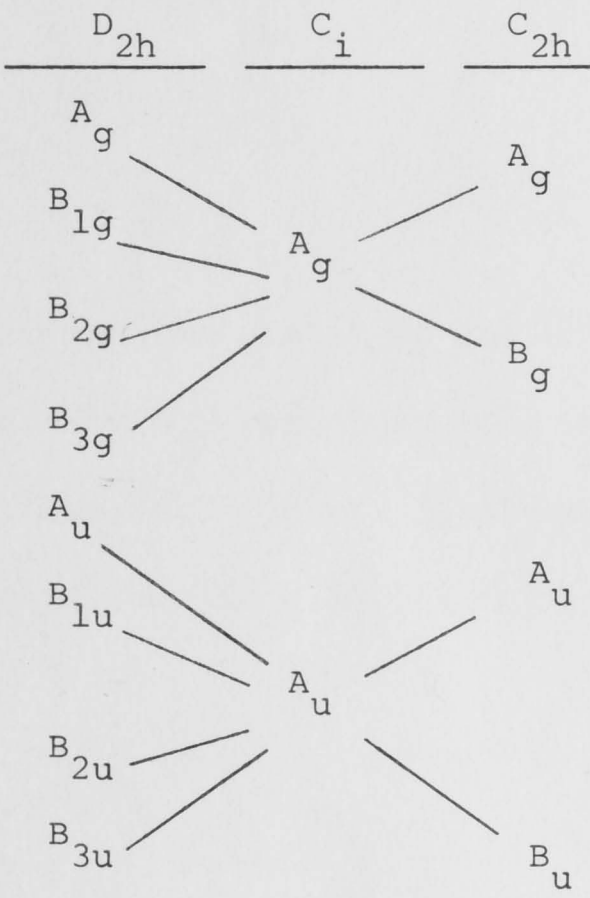
the symmetry properties of crystal wave functions can be associated with that of free molecular wave function.

The reciprocal lattice has the same underlying symmetry as the real lattice. The factor group analysis can be performed either on the real or on the Brillouin zone of the reciprocal lattice owing to the following relationship:

$$\underline{K} \cdot \alpha \underline{R}_{ip} = (\alpha^{-1} \underline{K} \cdot \underline{R}_{ip}) \qquad (2\text{-}11)$$

while α denotes a rotational operation. The latter route will be used here. If all the space group operations are carried out on a given wave vector in a reciprocal lattice, those operations that either leave $\underline{K}$ invariant or transfer it to an equivalent $\underline{K}$ (equivalent in a sense that it differs only by a lattice vector) will form a group called the group of the wave vector. But, in general, operating on a given wave vector, α will generate a set of different wave vectors, i.e., the star of $\underline{K}$. Degeneracies can therefore occur among those vectors associated together in the star, and for each member of the star, the crystal wave functions can be constructed through irreducible representation of the group of the wave vector. In one extreme case, namely, at a general point of the Brillouin zone, the group of the wave vector contains only the identity, so there is no symmetry operation that transform the crystal wave functions without changing $\underline{K}$. Consequently, the coefficients of B_i^r can not be found through symmetry consideration and must be obtained by diagonalization. In the other extreme case, at the centre of Brillouin zone ($\underline{K} = 0$), the group of the wave vector is identical with the factor group while the star contains only the zero vector, so that B_i can be found by symmetry consideration alone.

In anthracene (h = 2), for example, the factor group is C_{2h} with the identity (E), the twofold rotation (C_2^b), the inversion (i) and the reflection plane (σ_{ac}) as symmetry elements. Usually the twofold axis is labelled as the b axis and the symmetry plane is the ac plane. The vector is resolved into its components k_a, k_b and k_c along the crystal axes. At a general point, the star contains $(k_a, \bar{k}_b, k_c)$, $(\bar{k}_a, k_b, \bar{k}_c)$, $(\bar{k}_a, \bar{k}_b, \bar{k}_c)$ and (k_a, k_b, k_c), the group of K consists of the identity only. Therefore the classification of the wave functions by irreducible representations or the group of the wave vector is trivial. On the other hand, at $\underline{K} = 0$, the star contains the zero vector only, the group of K is C_{2h}, namely, the factor group. For anthracene crystal, the site group is C_i and the molecular point group is D_{2h}. Consequently, there is a correlation diagram as follows:



It can be seen that the factor group representations must have the same g or u character as the molecular wave functions and each molecular transition should give two bands (the factor-group components) in the crystal spectra. The crystal wave functions can be expressed as a linear combination of molecular wave functions,

$$\psi_{\alpha}^{r} = \sqrt{\frac{1}{2}} \left(B_1^{\alpha} \Phi_1^{r} + B_2^{\alpha} \Phi_2^{r} \right)$$

$$\psi_{\beta}^{r} = \sqrt{\frac{1}{2}} \left(B_1^{\beta} \Phi_1^{r} + B_2^{\beta} \Phi_2^{r} \right) \qquad (2\text{-}13)$$

These coefficients can be found as $B_1 = B_2 = 1$ for one branch and $B_1 = -B_2 = 1$ for the other.

2.3. First-order Perturbation Treatment

In total there are M crystal eigenfunctions for the r-th excited state. Correspondingly the eigenvalues can be, in principle, found by solving the secular equation which may be expressed as (2-14):

$$< \psi_i^r (\underline{K}) \Big| \sum_{ip} H_{ip} + \tfrac{1}{2} \sum_{ip \neq jq} V_{ip,jq} - E_i (\underline{K}) \Big| \psi_j^r (\underline{K}) > = 0 \qquad (2\text{-}14)$$

Using (2-2) and (2-7), this can be transformed to a hamiltonian matrix composing of N blocks of order h, each block associated with a particular value of $\underline{K}$. This may be expressed as:

$$\begin{vmatrix} \boxed{\underline{K} = 0} & 0 & 0 & - & - & - \\ 0 & \boxed{\underline{K} = \underline{K}_1} & 0 & - & - & - \\ 0 & 0 & \boxed{\quad} & - & - & - \\ 0 & 0 & 0 & - & - & - \\ - & - & - & - & - & - \end{vmatrix} = 0 \qquad (2\text{-}15)$$

If a number of excited states is included, the determinant of new secular equation would be extended to hxNxM, T being the number of excited states. However, for the first-order theory, it is assumed that the basis functions for different excited states are orthogonal:

$$< \psi^r(K) \Big| \psi^s(K) > = \delta_{rs} \qquad (2\text{-}16)$$

This is adequate for a strong transition such as the 2500 Å system of anthracene, but for a weak transition such as the 3800 Å system of anthracene, the condition (2-16) could not be applied and the interaction between different excited states must be included.

The solution of the secular equation (2-15) gives the transition energies from the ground state to the r-th excited state. The determinant has the following form:

1) Diagonal elements:

$$\Delta w^r + D^r + \sum_q{}' \exp\left(i\underline{K} \cdot (\underline{R}_{ip} - \underline{R}_{jq})\right) I^{rr}_{ip,jq} - E \qquad (2\text{-}17a)$$

2) Off-diagonal elements:

$$\sum_{jq}{}' \exp\left(i\underline{K} \cdot (\underline{R}_{ip} - \underline{R}_{jq})\right) I^{rr}_{ip,jq} \qquad (2\text{-}17b)$$

where

$$\Delta w^r = w^r - w^G$$

$$D^r = \sum_{jq}{}' \left[\langle \phi^r_{ip}\, \phi^G_{jq} | V_{ip,jq} | \phi^r_{ip} \phi^G_{jq} \rangle - \langle \phi^r_{ip} \phi^r_{jq} | V_{ip,jq} | \phi^G_{ip} \phi^G_{jq} \rangle \right]$$

$$I^{rr}_{ip,iq} = \sum_q \langle \phi^r_{ip} \phi^G_{iq} | V_{ip,iq} | \phi^G_{ip} \phi^r_{iq} \rangle$$

$$I^{rr}_{ip,jq} = \sum_q \langle \phi^r_{ip} \phi^G_{jq} | V_{ip,jq} | \phi^G_{ip} \phi^r_{jq} \rangle$$

Δw^r is the known free molecular transition energy

D^r is the change of van der Waals energy when a molecule is excited from its ground state to its r-th excited state while all others remain in the ground state. A point to bear in mind is that[25] D^r written in this form is a first order correction, whereas a part of the van der Waals' correction (i.e. the dispersion part) is second order. Thus one is writing D^r in a conventional way only. $I^{rr}_{ip,jq}$ is the resonance interaction between translationally equivalent molecules, $I_{ip,iq}$ is that between translationally inequivalent molecules. For anthracene, the eigenvalues corresponding to the $\underline{K} = 0$ transition are obtained as,

$$E_\alpha = w^r + D^r + I^{rr}_{ip,iq} + I^{rr}_{ip,jq}$$

$$E_\beta = w^r + D^r + I^{rr}_{ip,iq} - I^{rr}_{ip,jq} \qquad (2\text{-}18)$$

The energy difference, $E_\alpha - E_\beta$, is called the factor group splitting (Davydov splitting). Its magnitude depends on that of resonance interaction which is directional-dependent. Therefore, it is useful for comparison between experimental and calculated splitting to determine the symmetry of electronic transitions.

The optically allowed electronic transitions are those which satisfy the selection rules. The selection rules can be considered in two ways. On the one hand, it is required that the change in the wave vector between the initial and final state be equal to the wave vector of the absorbed light, i.e., $\underline{Q}$,

$$\Delta K = \underline{Q} \qquad (2\text{-}19a)$$

This is a consequence of the conservation of momentum in the absorption process. $Q = 2\Pi/\lambda$, λ being the wave length of the absorbed light. For visible or uv radiation, $\lambda \sim 10^{4}\,\text{Å}$, and Q is extremely small. (2.19a) may be replaced by (2-19b):

$$\Delta K = 0 \qquad (2\text{-}19b)$$

On the other hand, the transition moment for a crystal from the initial state to an excited state is expressed as,

$$M^r = \langle \psi_E | M | \psi_I \rangle \qquad (2\text{-}20)$$

in which $M = \sum_i \underline{e}\,\underline{r}_i$, $\underline{e}$ is the electronic charge and $\underline{r}$ is the position vector operator of the i-th electron. (2-20) will vanish unless the direct product of the symmetry representation of $\underline{\psi}_E$, $\underline{r}$ and $\underline{\psi}_I$ contains the totally symmetric representation of the group of the wave vector. For the absorption spectrum, the initial state is the

ground state in (2-1) which belongs to $\underline{K} = 0$, the totally symmetric representation. The argument now becomes that $\underline{r}$ should belong to the irreducible representation of the factor group because of (2-19) and because the group of the wave vector is the factor group itself in K = 0 case. Again, in anthracene, the factor group is C_{2h} and it can be seen that the condition is satisfied only for an excited state belonging to the A_u species (for $\underline{r}$ along $\underline{b}$ axis) and B_u species ($\underline{ac}$ plane). Light polarized in the $\underline{b}$ axis direction will be absorbed by the crystal in transitions to the excited state which belongs to A_u symmetry and in the $\underline{ac}$ plane direction to B_u symmetry. However, for general $\underline{K}$ the group of the wave vector is not the factor group. In fact, it has no elements other than the identity so the direction of polarization is unrelated to the crystal axes.

Also it is known that the intensity of the absorption band can be discussed in terms of the oscillator strength, f, which is proportional to the product of the square of the transition moment, $\underline{M}^2$, and transition frequency, E:

$$f \sim \underline{M}_r^2 \cdot E_i \tag{2-21}$$

in principle, the intensity ratio for f_{ac} and f_b is

$$\frac{f_{ac}}{f_b} = \frac{(\underline{M}_{ac}^r)^2}{(\underline{M}_b^r)^2} \cdot \frac{E_{ac}}{E_b} \tag{2-22}$$

However, the observations are taken, in practice, with light incident normal to the $\underline{ab}$ crystal plane so that the polarization ratio is actually defined as,

$$\frac{f_{ac}}{f_b} = \frac{(\underline{M}_{ac}^r \cdot \underline{a})^2}{(\underline{M}_b^r)^2} \frac{E_{ac}}{E_b} \tag{2-23}$$

$\underline{a}$ is the unit vector along the a crystal axis. If the difference

in transition frequencies between two Davydov components is not great, (2-23) can be replaced as,

$$\frac{f_a}{f_b} \simeq \frac{(\underline{M}^r_{ac} \cdot \underline{a})^2}{(\underline{M}^r_b)^2} \qquad (2\text{-}24)$$

Moreover, in the first order treatment, the oriented-gas model is used so that the molecules are assumed to be free from interaction. The transition moment is thus unchanged from free molecules to oriented-molecule crystal.

$$\underline{M}^r_{ac} + \underline{M}^r_b = \underline{M}^r \qquad (2\text{-}25a)$$

$$\frac{f_a}{f_b} = \frac{(\underline{M}^r \cdot \text{cosaM})^2}{(\underline{M}^r \cdot \text{cosbM})^2} \qquad (2\text{-}25b)$$

in which cosbM is a direction cosine. The polarization ratio depends only on the orientation parameters of the molecular crystal in the first order treatment.

2.4 Second-order Perturbation Treatment

To deal with weak transitions and real values of the polarization ratio, the theory can be refined by several considerations: one is the inclusion of higher terms in the multipole expansion during the evaluation of $I_{ip,iq}$ and $I_{ip,jq}$ sums. This will not be discussed in this thesis. Another is to allow the possibility of interaction between multiplets belonging to the same irreducible representation but different crystal excited states when the symmetry is lowered in going from the free molecule to the crystal. The effect of this interaction might be negligible for the case of strong transitions but probably not for the weak ones. Now the secular equation of (2-14) becomes,

$$\det \{ < \Phi_i^r (\underline{K}) \left| \sum_{ip} H_{ip} + \tfrac{1}{2} \sum_{ip,jq} V - E \right| \Phi_j^s (\underline{K}) > \} = 0 \quad (2\text{-}26)$$

The diagonal elements are unchanged from (2-17) but the off-diagonal terms have new integrals as,

$$H^{rs} = K^{rs} + J_{11}^{rs} + J_{12}^{rs} \quad (2\text{-}27)$$

with

$$K^{rs} = \langle \phi_{ip}^r \; \phi_{jq}^s \left| V_{ip,jq} \right| \phi_{ip}^G \; \phi_{jq}^G \rangle$$

$$J_{11}^{rs} = \langle \phi_{ip}^r \; \phi_{iq}^G \left| V_{ip,iq} \right| \phi_{ip}^G \; \phi_{iq}^s \rangle$$

$$J_{12}^{rs} = \langle \phi_{ip}^r \; \phi_{jq}^G \left| V_{ip,jq} \right| \phi_{ip}^G \; \phi_{jq}^s \rangle$$

For anthracene, Craig[1] had found that the value of K^{rs} intergrals vanish in the dipole approximation. The coupling of the weak 3800 Å with the strong 2500 Å system would be expressed as (2-28):

$$\begin{vmatrix} H^{rr}_{A_u} - E & & H^{rs}_{A_u} & 0 \\ 0 & H^{rr}_{B_u} - E & 0 & H^{rs}_{B_u} \\ H^{rs}_{B_u} & 0 & H^{ss}_{A_u} - E & 0 \\ 0 & H^{rs}_{B_u} & 0 & H^{ss}_{B_u} - E \end{vmatrix} = 0 \qquad (2\text{-}28)$$

in which

$$H^{rr}_{A_u} = E_\alpha$$

$$H^{rr}_{B_u} = E_\beta$$

$$H^{rs}_{A_u} = J^{rs}_{11} + J^{rs}_{12}$$

$$H^{rs}_{B_u} = J^{rs}_{11} - J^{rs}_{12}$$

When the condition $|H^{rr} - H^{ss}| >> H^{rs}$ holds, the second-order perturbation formula can be used to solve the above equation. It can be expressed,[3] for $E^r_{A_u}$, in a generalized form:

$$E^r_{A_u} = H^{rr}_{A_u} + \sum_s{}' \frac{(H^{rs}_{A_u})^2}{H^{rr}_{A_u} - H^{ss}_{A_u}} \qquad (2\text{-}29)$$

where s runs over all accessible transitions. There would be similar expressions for $E^r_{B_u}$, $E^s_{A_u}$ and $E^s_{A_u}$. The wave functions should also be in the form:

$$\underline{\psi}^{r'}_\beta = \underline{\psi}^r_\beta + \sum_s{}' \frac{H^{rs}_\beta}{H^{rr}_\beta - H^{ss}_\beta} \underline{\psi}^s_\beta \qquad (2\text{-}30)$$

where β denotes A_u or B_u component. The intensities should also be re-distributed and the transition moment per unit cell may be expressed as (2-31):

$$\underline{M}^{r'} = \underline{M}_{\beta}^{r} + \sum_{s}{}' \frac{H_{\beta}^{rs}}{H_{\beta}^{rr} - H_{\beta}^{ss}} \underline{M}_{\beta}^{s} \qquad (2\text{-}31)$$

Substituting this improved value of the transition moment, the polarization ratio can be re-calculated using (2-31).

The coupling with more than one accessible electronic transition could also be included in the treatment. In the case of anthracene, there have been reported about the 2200Å and 1800Å band systems but there is no definite assignment yet.

After Craig's successful interpretation[1,2] of the optical spectra, the 2500Å and 3800Å band systems of crystalline anthracene have been used as a prototype, because the known crystal structure and polarization allows one to make a comparison between theory and experiment as well as between the old and new treatments. In recent research, there is a new treatment using the approximate second quantization method. It is the aim of the next chapters to discuss this new method in comparison with the present treatment.

CHAPTER 3

Theory of Molecular Crystal in Occupation Number Representation

3.1 Introduction

The second quantization method has been employed by Hopfield,[6] Agranovitch,[7,8] Craig and Dissado[9] and many other investigators[10] to study exciton phenomena in molecular crystals. For a formal presentation of this method, there are several texts available such as Tyablikov's[11] and Power's.[12] In this chapter, only those topics which relate to the present study will be briefly reviewed. Let h, N, M, ip etc., retain their definitions as in Chapter 2. The essence of the second quantization method is the use of creation and annihilation operators in the occupation number representation. The occupation number, $n_{ip,f}$, is introduced to indicate whether the ip-th site molecule is in the f-th state or not (f can be the ground or any one of the excited states). When the ip-th molecule is, for example, in the ground state, $n_{ip,G} = 1$ and $n_{ip,r} = n_{ip,s} = 0$ (r and s denote the excited states. This is consistent with the fact that each molecule can be in only one state. When f runs over all possible states of the molecule at the ip-th site,

$$\sum_{f} n_{ip,f} = 1 \tag{3-1}$$

and ip over all sites of the crystal,

$$\sum_{ip} \sum_{f} n_{ip,f} = M \tag{3-2}$$

To simplify the argument, only one excited state will be considered in this chapter so that f = G or r only.

The occupation number representation of the crystal ground state of (2-1) is,

$$\left| 1, o, 1, 0 \ldots\ldots\ldots \; 1, 0. \ldots\ldots\ldots 1, 0 \right> \qquad (3\text{-}3)$$

corresponding to

$$\left| n_{11,G'} \; n_{11,r} \ldots\ldots\ldots n_{ip,G'} \; n_{ip,r} \ldots\ldots n_{hN,G'} \; n_{hN,r} \right>$$

When the ip-th site is excited to its r-th excited state, all others are in the ground state, the localized wave function may be expressed in the occupation number representation as,

$$\left| \Phi^{r}_{ip} \right> = \left| 1, 0, \ldots\ldots\ldots 0, 1, \ldots\ldots\ldots 1,0 \right> \qquad (3\text{-}4)$$

corresponding to (2-5). The above expression can be simplified by introducing creation and annihilation operators which are defined as,

$$b^{+}_{ip,f} \left| \psi \right> = \sqrt{1-n_{ip,f}} \left| n_{11,G} \ldots\ldots, n_{ip,f}{}^{+1}, \ldots \right>$$

$$b_{ip,f} \left| \psi \right> = \sqrt{n_{ip,f}} \left| n_{11,G} \ldots\ldots, n_{ip,f}{}^{-1}, \ldots \right> \qquad (3\text{-}5)$$

The definition omitted a factor of $\pm$ 1 which is necessary when antisymmetrization is taken into account. Since there is only one molecule in each site and this molecule must be in one state or another, $n_{ip,f}$ can be only 1 or 0. Accordingly, the results of operation, $\sqrt{1 - n_{ip,f}}$ and $\sqrt{n_{ip,f}}$ can be replaced by $1 - n_{ip,f}$ and $n_{ip,f}$ respectively. It can be seen that, under the operation $b^{+}_{ip,f}$, the number of particles (in this case, "particle" means "state occupation") in the f-th state of ip-th site is increased by unity; if there is already a particle there, the result of operation, $1 - n_{ip,f}$, gives zero. On the other hand, the number of particles in the f-th

state of the ip-th site is decreased by unity by $b_{ip,f}$ and if there was no particle before the operation, the result, $n_{ip,f}$, yields zero. It follows that,

$$b^{+}_{ip,f} \; b^{+}_{ip,f} \left| \psi > \right. = 0$$

$$b_{ip,f} \; b_{ip,f} \left| \psi > \right. = 0 \qquad (3\text{-}6a)$$

Also there are two combined operators defined as,

$$b^{+}_{ip,f} \; b_{ip,f} \left| \psi > \right. = N'_{ip,f} \left| \psi > \right.$$

$$b_{ip,f} \; b_{ip,f} \left| \psi > \right. = N''_{ip,f} \left| \psi > \right. \qquad (3\text{-}6b)$$

The wave function is unchanged by the operation of $b^{+}_{ip,f} \; b_{ip,f}$ and $b_{ip,f} \; b^{+}_{ip,f}$. The former is called the number operator because when acting on the f-th state of the ip-th site, it yields the number of molecules in the f-th state. On the other hand, $b_{ip,f} \; b^{+}_{ip,f}$ yields the number of molecules not in the f-th state of the ip-th site. There is only one molecule in each site and this molecule must in one state or another, it follows that,

$$b^{+}_{ip,f} \; b_{ip,f} + b_{ip,f} \; b^{+}_{ip,f} = N'_{ip,f} + N''_{ip,f} = 1 \qquad (3\text{-}6c)$$

(3-6c), together with (3-6a & 3-6b) is called the fermion commutation rules.

Now (3-4) can be re-expressed in terms of the creation and annihilation operators as,

$$\left| \psi^{r}_{ip} > \right. = b^{+}_{ip,r} \; b_{ip,G} \left| \psi^{G} > \right. \qquad (3\text{-}7)$$

On the other hand, the ground state wave function may also be re-expressed as,

$$\left| \psi_G^{>} \right. = b^{+}_{ip,G} \; b_{ip,r} \left| \Phi^{r}_{ip} \right> \qquad (3\text{-}8a)$$

It is convenient to define another particular state called the "vacuum state" in which there are no particles. The crystal ground state is generated by the vacuum state, $|0>$,

$$\left| \psi^{G}_{>} \right. = \prod_{ip} b^{+}_{ip,G} \left| 0 > \right. \qquad (3\text{-}8b)$$

It is important to note that,[25] in the occupation number representation, the molecules are there always, but may be in no state (if all molecules are in no state, the system is in the vacuum state), otherwise a molecule is in one state or another. From this point of view, one ought to speak of the operators, b^{+} and b as changing the occupation of a given state of a given molecule and not as creating or destroying molecules.

In Chapter 2, the system hamiltonian of a molecular crystal is written in the form:

$$H = \sum_{ip} H_{ip} + \tfrac{1}{2} \sum_{ip \neq jq} V_{ip,jq} \qquad (2\text{-}3)$$

and the Schrodinger equation as,

$$< \psi_i \left| \sum_{ip} H_{ip} + \tfrac{1}{2} \sum_{ip \neq jq} V_{ip,jq} \right| \psi_j > = E < \psi_i | \psi_j > \qquad (2\text{-}14)$$

Corresponding to (2-14), there is a second-quantization representation:

$$H = H_1 + H_2 \qquad (3\text{-}9)$$

where $H_1 = \sum_f \sum_{ip} w^f b^+_{ip,f} b_{ip,f}$

$$H_2 = \sum_{\substack{f_1 f_2 \\ f'_1 f'_2}} \sum_{ip \neq jq} v_{ip,jq} b^+_{ip,f_1} b^+_{jq,f_2} b_{ip,f'_2} b_{jq,f'_2}$$

In the zeroth order approximation, the molecular crystal is treated as a system of non-interacting oriented molecules so H is just the H_1 term in (3-9). Consequently, the energy operator H is already in a diagonal form as,

$$H = \sum_f \sum_{ip} w^f b^+_{ip,f} b_{ip,f}$$

$$= \sum_f \sum_{ip} w^f N'_{ip,f}$$

$$= \sum_f w^f N_f \qquad (3\text{-}10)$$

because of (3-6). N_f is the total number of $N'_{ip,f}$. $\sum_f N_f$ must equal to M because of (3-2). In other words, the total number operator, $\sum_f \sum_{ip} b^+_{ip,f} b_{ip,f}$, must commute with the energy operator H and the total number of "particles" in the system is a constant. This is connected with the fact that each time the number of particles in one state is decreased by unity, the number of particles in another state is increased by unity

For a real system of a molecular crystal, the total number operator no longer commutes with the energy operator. This is due to the appearance of the cross term in (3-13). The study of the energy states of a molecular crystal becomes that of finding a new set of creation (A^+) and annihilation (A) operators which will take into account the interaction term and becomes,

$$H = \sum_i E_i A^+_i A_i \qquad (3\text{-}11)$$

(3-11) is in diagonal form and the energy eigenvalues, E_i, can read off from it.

3.2 Approximate Second Quantization Method

A method was developed by Bogoliubov[13] to diagonalize the energy operator of (3-9) into (3-11). This method is often called the "approximate" second quantization method. Its basic idea is to transform (3-9) which desecribing a system of many interacting particles to an energy operator describing a system of non-interacting pseudo-particles in terms of pseudo-particle creation and annihilation operators. The starting point is to define the combined operators, $b^{+}_{ip,r}\, b_{ip,G}$ and $b^{+}_{ip,G}\, b_{ip,r}$ as the excitation creation and annihilation operators respectively,

$$B^{+}_{ip,r} = b^{+}_{ip,r}\, b_{ip,G} \qquad (3\text{-}12)$$

$$B_{ip,r} = b^{+}_{ip,G}\, b_{ip,r}$$

The physical picture of $B^{+}_{ip,r}$ is the transition of molecule at the ip-th site from its ground state to r-th excited state and the operator $B_{ip,r}$ is the reverse physical process so as to transfer molecule at the ip-th site from its r-th excited state to the ground state. It should be noted that these are the creation and annihilation operators of excitations in molecules and should not be confused with the creation and annihilation operators of the state occupation of a given state of a given molecule. $B^{+}_{ip,r}$ and $B_{ip,r}$ may be called "pseudo-particles" creation and annihilation operators respectively because these operators do not deal with the real particles but rather with the pseudo-particles, i.e., excitations. Although the pseudo-particle shares some properties with the real particle such as wave-particle duality, there are differences in certain ways. One of them is the contents of vacuum state. For the excitation vacuum state, it is not $|0\rangle$ defined in (3-8b) but

rather $| \psi^G >$, namely, the crystal ground state in which there are no excitations at all. This difference is important for later discussion. Another difference is the commutation rules obeyed. For molecules in crystal they are fermions because of (3-6), so are the excitations because of (3-12). However, it is found that for a low concentration of excitations in crystal, the commutation rules for the excitations can be transformed from that of fermions to bosons. This can be discussed via the number operators. The exciton number operators are the combined operators of $B^+_{ip,r}$ and $B_{ip,r}$ which by acting on the crystal wave function give the eigenvalues N' and N";

$$B^+_{ip,r} B_{ip,r} | \psi > = N' | \psi > \qquad (3\text{-}13a)$$

$$B_{ip,r} B^+_{ip,r} | \psi > = N'' | \psi >$$

By writing down the operations explicitly in terms of $b^+_{ip,r}$ and $b_{ip,r}$, one has (3-13b);

$$B^+_{ip,r} B_{ip,e} | \psi > = b^+_{ip,r} b_{ip,G} b_{ip,G} b_{ip,r} | \psi >$$

$$= (1-N_{ip,G}) N_{ip,r} \qquad (3\text{-}13b)$$

$$B_{ip,r} B^r_{ip,r} | \psi > = N_{ip,G} (1-N_{ip,r})$$

For ultra-violet radiation of low intensity, only a small number of molecules in a molecular crystal are excited. The average $N_{ip,r}$ over the whole lattice is extremely small and can be considered as zero while the average $N_{ip,G}$ can be considered as unity because each molecule must be in one state or another so that,

$$< N_{ip,G} > \sim 1$$

$$< N_{ip,r} > \sim 0 \qquad (3\text{-}14)$$

By substituting (3-14) into (3-13a), it follows that,

$$< N' > \sim 0$$

$$< N'' > \sim 1 \qquad (3\text{-}15)$$

and

$$B^{+}_{ip,r} B_{ip,r} + B_{ip,r} B^{+}_{ip,r} = 1$$

$$B^{+}_{ip,r} B^{+}_{ip,r} = 0 \qquad (3\text{-}16)$$

$$B_{ip,r} B_{ip,r} = 0$$

because of (3-14) and (3-6). Formula (3-16) is the fermion commutation rules.

It is interesting to see that, when $ip \neq jq$,

$$B_{ip,r} B_{jq,r} - B_{jq,r} B_{ip,r} = 0 \qquad (3\text{-}17a)$$

$$B^{+}_{ip,r} B^{+}_{jq,r} - B^{+}_{jq,r} B^{+}_{ip,r} = 0 \qquad (3\text{-}17b)$$

$$B_{ip,r} B^{+}_{jq,r} - B^{+}_{jq,r} B_{ip,r} = 0 \qquad (3\text{-}17c)$$

When $ip = jq$, (3-17a) and (3-17b) remain valid, but not for (3-17c) which becomes, by using (3-13) and (3-15):

$$B_{ip,r} B^{+}_{ip,r} - B^{+}_{ip,r} B_{ip,r} = (1 - B^{+}_{ip,r} B_{ip,r}) - B^{+}_{ip,r} B_{ip,r}$$

$$= 1 - 2\, B^{+}_{ip,r} B_{ip,r}$$

$$= 1 - 2\, N' \qquad (3\text{-}18a)$$

or equivalently,

$$B_{ip,r} B^{+}_{ip,r} - B^{+}_{ip,r} B_{ip,r} = B_{ip,r} B^{+}_{ip,r} - (1 - b_{ip,r} B^{+}_{ip,r})$$

$$= 2\, B_{ip,r} B^{+}_{ip,r} - 1$$

$$= 2\, N'' - 1 \qquad (3\text{-}18b)$$

By substituting (3-15) into (3-18), the right hand sides of (3-18) always become 1. Combining with (3-17), the commutator leads to that for bosons:

$$B_{ip,r} B^{+}_{jq,r} - B^{+}_{jq,r} B_{ip,r} = [B_{ip,r}, B^{+}_{jq,r}] = \delta_{ip,jq}$$

$$[B^{+}_{ip,r}, B^{+}_{jq,r}] = 0 \qquad (3\text{-}19)$$

$$[B_{ip,r}, B_{jq,r}] = 0$$

Obviously, the change from fermion to boson commutator is only approximate. It should be noted that, once the boson properties are assigned to the excitation operators, the occupation number and eigenvalues can have values more than the real ones (0 or 1). In the language of approximate second quantization it means the "non-physical" state are introduced which leads to a certain error. However, the error may be small because the total number of excitation present in the system is small in view of (3-13) and the chance of two or more excitations coinciding at one site is negligible.

3.3 Exciton Energy Operator of Molecular Crystal

In terms of new boson operators, B^+ and B, (3-7) and (3-8a) can be written as,

$$| \Phi^r_{ip} > = B^+_{ip,r} | \Psi^G > \qquad (3\text{-}20a)$$

$$| \Psi^G > = B_{ip,r} | \Phi^r_{ip} > \qquad (3\text{-}20b)$$

also, corresponding to (2-6), a delocalized wave function can be expressed as,

$$\psi^r(\underline{k}) = \sqrt{\frac{1}{N}} \sum_{ip} \exp\ (i\ \underline{K}.\underline{R}_{ip})\ B^+_{ip,r} \mid \Psi^G >$$

$$= B^r_{k,h,r} \mid \Psi^G > \qquad (3\text{-}21)$$

$$\text{with } B^+_{k,h,r} = \sqrt{\frac{1}{N}} \sum_{ip} \exp\ (i\underline{k}.\underline{R}_{ip})\ B^+_{ip,r} \qquad (3\text{-}22a)$$

k is the wave vector for the r-th excitation. It follows that,

$$B_{k,h,r} = \sqrt{\frac{1}{N}} \sum_{ip} \exp\ (-i\underline{K}.\underline{R})\ B_{ip,r} \qquad (3\text{-}22b)$$

the distribution of k signs are necessary to keep the invariance to translation. $B^+_{k,h,r}$ and $B_{k,h,r}$ may be called the delocalized excitation (exciton) creation and annihilation operator respectively. Its number operator yields,

$$B^+_{k,h,r}\ B_{k,h,r} = \sqrt{\frac{1}{N}} \sum_{ip} B^+_{ip,r}\ B_{ip,r}$$

$$= \sqrt{\frac{1}{N}} \sum_{ip} N'_{ip} \qquad (3\text{-}22c)$$

because of (3-13). It is very important to note that although the average N' over the whole lattice is considered as zero in (3-4), the total number of excitation, $\sum_{ip} N'_{ip}$, is not zero. In fact, it is

a variable rather than a constant, in contrast to the total number of real particles, because there is no such condition as (3-2) imposed. However, for a stationary state of a molecular crystal,

$$\sum_{ip} N'_{ip} \ll M \qquad (3\text{-}23)$$

so that (3-14) can hold true. Otherwise, one of the main concepts of the approximate second quantization method would break down.

The matrix element, $< f_1 f_2 \mid V \mid f_1' f_2' >$ represents the interaction of transition moments between the ip-th and jq-th molecule in the multipole approximation of V in (3-9). It involves many combinations for all available electronic states. By separating the various types of these matrix elements, the following combinations are of interest:

a) the interaction between molecules in the ground state represented as $< G\ G \mid V \mid G\ G >$;

b) the interaction between an excited molecule and un-excited one represented as $< G\ r \mid V \mid r\ G >$;

c) the interaction between a molecule excited to the excited state and another de-excited to the ground state is expressed as $< G\ r \mid V \mid G\ r >$;

d) the interaction between two molecules simultaneously excited as well as between two molecules de-excited represented by $< G\ G \mid V \mid r\ r >$ and $< r\ r \mid V \mid G\ G >$;

e) the interaction forms expressed as, $< G\ r \mid V \mid r\ r >$ or $< r\ r \mid V \mid r\ r >$ etc..

Again, consider the condition (3-14), the contribution of type (e) is sufficiently small comparing with that of other types and is neglected hereafter.

Now, the exciton energy operator of the molecular crystal can be readily formulated (see References 4 and 8). The derivation will be discussed in detail later. The energy operator takes the form as,

$$H_{total} = H_0 + H_1 + H_2 + H_3 \qquad (3\text{-}25)$$

where

$$H_0 = Mw^r + \tfrac{1}{2} \sum_{ip,jq} < G\ G\ |V|\ G\ G >$$

$$H_1 = \sum_{ip} (\Delta w^r + D^r)\ B^+_{ip,r}\ B_{ip,r}$$

$$D^r = \sum_{jq} (< G\ r\ |V|\ r\ G > - < G\ G\ |V|\ G\ G >)$$

$$H_2 = \sum_{ip,jq} L^r_{ip,jq}\ b^+_{ip,r}\ b^+_{jq,G}\ b_{ip,G}\ b_{jq,r}$$

$$= \sum_{ip,jq} L^r_{ip,jq}\ B^+_{ip,r}\ B_{jq,r}$$

$$H_3 = \tfrac{1}{2} \sum_{ip,jq} M^r_{ip,jq} (b^+_{ip,r}\ b^+_{jq,r}\ b_{ip,G}\ b_{jq,G} + b^+_{ip,G}\ b^+_{jq,G}\ b_{ip,r}\ b_{jq,r})$$

$$+ \tfrac{1}{2} \sum_{ip,jq} M^r_{ip,jq} (B^+_{ip,r}\ B^+_{jq,r} + B_{ip,r}\ B_{jq,r})$$

$$L^r_{ip,jq} = < G\ r\ |V_{ip,jq}|\ G\ r > \qquad \text{type (c)}$$

$$M^r_{ip,jq} = < G\ G\ |V_{ip,jq}|\ r\ r > = < r\ r\ |V_{ip,jq}|\ G\ G > \qquad \text{type (d)}$$

If H_o, which represented the ground state energy, can be considered as the reference energy, the exciton energy operator becomes,

$$H = H_{total} - H_0$$

$$= H_1 + H_2 + H_3$$

$$= \sum_{ip} (\Delta w^r + D^r) B^+_{ip,r} B_{ip,r} + \sum_{ip,jq} L^r_{ip,jq} B^+_{ip,r} B_{jq,r}$$

$$+ \tfrac{1}{2} \sum_{ip,jq} M^r_{ip,jq} B^+_{ip,r} B^r_{jq,r} + \tfrac{1}{2} \sum_{ip,jq} M^r_{ip,jq} B_{ip,r} B_{jq,r} \qquad (3\text{-}26)$$

When this energy operator, H, is diagonalized, the eigenvalues can be read off from the diagonal form like (3-10). H_1 term represents the free molecule excitation energy with modifying terms for the dispersion energies of the ground and excited states. H_2 describes the creation of one excitation and the simultaneous destruction of the other. H_3 is the simultaneous creation or annihilation of two excitation particles. In principle, there would be an H_4 term describing the combination of B and B^+ in powers higher than two (type (e)). But, as mentioned earlier, it is dropped in view of (3-14). In fact, this is one of the conditions for the application of the approximate second quantization method because the Bogoliubov-Tyablikov transformation can only diagonalize an energy operator in quadratic form. Another condition is that of (3-14) which has already employed extensively. In some treatments,[4,10] it is further assumed that matrix element, $L^r_{ip,jq}$ and $M^r_{ip,jq}$ are equal to one another. This will be discussed later and will not be used here because without this approximation, the energy operator can still be diagonalized.

The delocalized exciton creation and annihilation operators can now be employed to express the energy operator in the form,

$$H = \sum_{k,h} (\Delta w + D)\, B^{+}_{k,h} B_{k,h} + \sum_{k,h,h'} L_{h,h'} B^{+}_{k,h} B_{-k,h'}$$

$$+ \tfrac{1}{2} \sum_{k,h,h'} M_{h,h'} (B^{+}_{k,h} B^{+}_{-k,h'} + B_{-k,h} B'_{k,h'}) \qquad (3\text{-}26a)$$

Since only one excited state is of interest, the subscript r can be dropped.

3.4 Bogoliubov-Tyablikov Canonical Transformation

The basic procedure of the Bogoliubov-Tyablikov canonical transformation[11,13] is a mixing of operators B^+ and B in (3-26) to give new boson operator A and A^+ so that the off-diagonal part of (3-26) can be made to vanish and the energy operator reduces to the form as (3-11). This is called the Bogoliubov-Tyablikov transformation:

$$B_{k,h} = \sum_i (U_{hi} A_{k,i} + V^*_{hi} A^+_{-k,i})$$

$$B^+_{-k,h} = \sum_i (U^*_{hi} A^+_{-k,i} + V_{hi} A_{k,i}) \qquad (3\text{-}27)$$

Its reverse transformation has the form:

$$A_{k,h} = \sum_h (U^*_{hi} B_{k,h} - V^*_{hi} B^+_{-k,h})$$

$$A^+_{-k,h} = \sum_h (U_{hi} B^+_{-k,h} - V_{hi} B_{k,h}) \qquad (3\text{-}28)$$

In order to satisfy both (3-27) and (3-28), the eigen-functions U and V must obey the following condition:

$$\sum_i (U_{h,i} U^*_{h'i} - V_{h'i} V^*_{hi}) = \delta_{h\,h'}$$

$$\sum_i (U_{h'i} V^*_{hi} - U_{hi} V^*_{h'i}) = 0 \qquad (3\text{-}29)$$

Also, to make the transformation canonical, the operators A and A^+ must satisfy the boson commutation rules like B and B^+. The commutators are found as,

$$A_{ki} A^+_{-kj} - A^+_{-kj} A_{ki} = [A_{ki}, A_{-k,j}] = \delta_{ij}$$

$$A_{ki} A_{-kj} - A_{kj} A_{ki} = 0 \qquad (3\text{-}30)$$

$$A^+_{ki} A^+_{-ki} - A^+_{kj} A^+_{-ki} = 0$$

because of (3-29). In other words, the Bogoliubov-Tyablikov transformation, its reverse transformation together with the condition (3-29) guarantee that the new operators are bosons. Moreover, the operators A and A^+ are new because they represent the creation and annihilation operators of a system of independent pseudo-particles and unlike operator B and B^+ which representing those of interacting system. Consequently, the total number operators must commute with the energy operator and the number of "pseudo-particles" is a constant of motion after transformation. In the language of Heisenberg representation, this means that A and A^+ must satisfy the following equations of motion as,

$$i \frac{d}{dt} A_{ki} = E_i A_{ki}$$

$$i \frac{d}{dt} A^+_{-ki} = E_i A^+_{-ki} \qquad (3\text{-}31a)$$

so that

$$i \frac{d}{dt} \left(\sum_h \left(U^*_{hi} B_{k,h} - V_{hi} B^+_{-k,h}\right)\right) = E_i \left(\sum_h \left(U^*_{hi} B_{k,h} - V_{k,h} B^+_{-k,h}\right)\right)$$

$$i \frac{d}{dt} \left(\sum_h \left(U_{hi} B^+_{-k,h} - V_{hi} B_{k,h}\right)\right) = -E_i \left(\sum_h \left(U_{hi} B^+_{-k,h} - V_{hi} B_{k,h}\right)\right) \qquad (3\text{-}31b)$$

On the other hand, the equations of motion for B and B^+ have the form:

$$i \frac{d}{dt} B_{k,h} = [B_{k,h'}, H] = ((\Delta w + D) + \sum_{h'} L_{hh'}) B_{k,h} + \sum_{h'} M_{hh'} B^+_{-k,h}$$

$$i \frac{d}{dt} B^+_{-k,h} = [B^+_{-k,h'}, H] = ((\Delta w + D) + \sum_{h'} L_{hh'}) B^+_{-k,h} + \sum_{h'} M_{hh'} B_{k,h'} \qquad (3\text{-}32)$$

Substituting (3-32) into (3-31b) and using the fact that the operators A and A^+ are linearly independent so their coefficients should vanish independently of one another, one obtains,

$$E_i U_{hi} = ((\Delta w + D) + \sum_{h'} L_{hh'}) U_{kh} + \sum_{h'} M_{hh'} V_{kh'}$$

$$-E_i V_{hi} = ((\Delta w + D) + \sum_{h'} L_{hh'}) V_{kh} + \sum_{h'} M_{hh'} U_{kh'} \qquad (3\text{-}33)$$

(3-33) may be called the Tyablikov equations. It determines the relationship between eigenvalues, E_i, and eigenfunctions. After substituting (3-27) into (3-26), one obtains (see Reference 11),

$$H = \Delta E + \sum_{k,i} E_i A^+_{ki} A_{ki} \qquad (3\text{-}26b)$$

with

$$\Delta E = -\sum_{k,i,h} E_i V^*_{hi} V_{hi}$$

ΔE_i is a small correction term. To be precise, E_i, ΔE, V_{hi} and V_{hi} should be in the form $E_i(k)$, $E(k)$, $U_{hi}(k)$ and $V_{hi}(k)$ with k as the wave vector of the r-th excitation. This will be discussed later. One can see that (3-26b) is in diagonal form after the Bogoliubov-Tyablikov transformation so long as the eigenvalues and eigenfunctions satisfy the Tyablikov equations in (3-33). It should be noted that the number of eigenvalues is even because the functions U and V occur in pairs. The eigenvalues which are less than zero are rejected. It is interesting to note that during this diagonalization, no perturbation-expansion is involved.

It is appropriate to write down the explicit form of (3-33) for the case of h = 1 and 2 respectively.

Case (1) $h = 1$

$$[\Delta w + D - E(k)] \quad U(k) + L(k) \quad [U(k) + V(k)] = 0$$

$$[\Delta w + D + E(k)] \quad U(k) + L(k) \quad [U(k) + V(k)] = 0 \qquad (3\text{-}34a)$$

Case (2) $h = 2$

$$[\Delta w + D + L_{11}(k) - E(k)] \quad U_{11}(k) + L_{12}(k)\, V_{11}(k) + M_{12}$$

$$[U'_{11}(k) + V_{11}(k)] = 0$$

$$L_{12}\, U_{12}(k) + [\Delta w + D + L_{11}(k) + E(k)]\, V_{12}(k) + M_{12}(k)$$

$$[U_{12}(k) + V_{12}(k)] = 0$$

$$M_{21}(k)\, [U_{21}(k) + U_{21}(k)] + [\Delta w + D + L_{22}(k)] - E(k)$$

$$U_{21}(k) + L_{21}(k)\, V_{21}(k) = 0$$

$$M_{21}(k)\, [U_{22}(k) + V_{12}(k)] + L_{21}(k) \quad U_{22}(k) + [\Delta w + D + L_{22}(k)]$$

$$+ E(k)]\, V_{22}(k) = 0$$

(3-34b)

The result can be made identical with that in Chapter 2 if the two-exciton term, H_2, in (3-26) is neglected[4] in the first instance. The energy operator becomes,

$$H = \sum_{k,h} (\Delta w + D) \quad B^{+}_{k,h}\, B_{-k,h} + \sum_{k,h,h'} L_{hh'}\, B^{+}_{k.h}\, B_{-k,h'} \qquad (3\text{-}35)$$

This expression will be discussed in the next Chapter more carefully. One can see that the number operator commutes with the energy operator even before any transformation and the total number of excitations is conserved. The energy operator can then be diagonalized using a unitary transformation, instead of the Bogoliubov-Tyablikov canonical transformation, as,

$$B_{k,h} = \sum_i U^*_{hi} A_{k,i} \tag{3-36}$$

with the condition that A^+ and A are bosons so that,

$$A_{ki} A^+_{-kj} - A^+_{-kj} A_{ki} = [A_{ki} A^+_{-kj}] = \delta_{ij} \tag{3-37}$$

with the condition that the eigenvalues relate with the eigenfunctions by,

$$\sum_{h'} [(\Delta W + D) \delta_{hh'} + L_{hh'}] U_{h'i} = E_i U_{hi} \tag{3-38}$$

The energy operator is in diagonal form:

$$H = \sum_{k,i} E_i A^+_{ki} A_{-ki} \tag{3-39}$$

with respect to the new operators A^+_{ki} and A_{ki}.

For the case of h = 2, the explicit form of (3-38) is,

$$[\Delta w+D + L_{11}(k) - E(k)] U_{11}(k) + L_{12}(k) U_{12}(k) = 0$$

$$L_{21}(k) U_{21}(k) + [\Delta w+D + L_{22}(k) - E(k)] U_{22}(k) = 0 \tag{3-40}$$

This is identical with the result in Chapter 2 in view of (2-17) in which only K = 0 is considered.

CHAPTER 4

First Comparison Between the Two Representations

4.1 Unitary Equivalence

The exciton theory of molecular crystals by the Frenkel-Davydov-Craig theory, and by the approximate second quantization, has been briefly reviewed in Chapters 2 and 3 respectively. The treatment of Chapter 2 may be said to be in the co-ordinate representation while that of Chapter 3 in the occupation number representation. It is seen that the latter differs from the former in that it avoids the procedure of perturbation expansion. The energy levels of a molecular crystal can be found by diagonalizing the exciton energy operator using the Bogoliubov-Tyablikov transformation. The object of this chapter is to make a comparison between these two representations.

One obvious approach is to find out whether or not there is a "unitary equivalence" relationship between them. Two representations are unitary equivalent if they are related by a unitary transformation, U, as,

$$A = U A' U^{-1}$$

$$\Phi = U \Phi' \qquad (4\text{-}1)$$

$$\Sigma\, U\, U^{*} = 1$$

$$U^{*} = U^{-1}$$

A, A' and Φ, Φ' are operators and wave functions respectively before and after unitary transformation. If these representations are related by (4-1), it will make no difference in physical prediction which representation is being used, the resulting eigenvalues will be the same except, trivially, for the notation being used in the two

representations and for the order in which they are arranged. However, in the present case, the treatment in the occupation number representation is based on the approximate second quantization method. By saying "approximate", one is referring to the change from fermion to boson character (see (3-19)) and the condition applicable only to the ground state and weakly excited states of the system (see (3-14)). Moreover, it involves the use of the Bogoliubov-Tyablikov canonical transformation instead of the unitary one, and the appearance of some interaction terms which do not have a conventional equivalence because the operators, B B and $B^{+}B^{+}$, do not conserve the number of particles. In view of these changes, one would hardly expect that unitary equivalence can be established between the two representations. This could be confirmed by deriving the energy operator in (3-26) of the occupation number representation from (2-1) of the co-ordinate representation explicitly. It is interesting to note that, in the application of the approximate second qunatization method to the exciton problem of molecular crystals, this derivation has not been done before. In the theory of metals, it was done by Bogoliubov[13] and in the theory of non-linear effects in crystals, it was done by Lalovic, Tosic and Zakula.[27] Both are at a sophisticated level. The purpose of the next section is to carry out the derivation in an elementary way.

4.2 Derivation of Energy Operator

The energy operator can be written in the form:

$$H = \sum_{ip} H_{ip} + \tfrac{1}{2} \sum_{ip,jq} V_{ip,jq} \qquad (2\text{-}1)$$

Within the limit of two-particle interactions, (2-1) can be re-expressed in the second quantization representation as (5-2):

$$H = \sum \langle f_1 | H_{ip} | f_1' \rangle \, b^{+}_{ip,f_1} \, b_{ip,f_1'} \qquad (4\text{-}2)$$

$$+ \tfrac{1}{2} \sum_{\substack{ip,jq \\ f_1,f_2 \\ f_1',f_2'}} \langle f_1 \, f_2 | V_{ip,jq} | \, f_1' \, f_2' \rangle \, b^{+}_{ip,f_1} \, b^{+}_{jq,f_2} \, b_{ip,f_1'} b_{jq,f_2}$$

For simplicity, the case of h = 1 will be used in the following derivation so that i = j = 1 and the subscripts ip(jq) are changed to p(q). The summation of p and q runs over all lattice sites except for p = q, and f_1, f_2, f_1' and f_2' over all electronic states in which only G (the ground state) and r (the r-th excited state) are included in the present discussion. The definition of $b^{+}_{p,r}$ and $b_{q,G}$ can be seen in Sec. 3.1.

Following Bogoliubov, a new set of creation, $b^{+'}$, and annihilation, b', operators is introduced which are related to the original ones, b^{+} and b, by means of a unitary transformation:

$$b_{p,G} = \theta_p(G,G) \, b'_{p,G} + \theta_p(r,G) \, b'_{p,r} = \sum_g \theta_q \, (g,G) \, b'_{p,g} \qquad (4\text{-}3)$$

$$b^{+}_{q,r} = \sum_g \theta^{*}_q \, (g,r) \, b^{+'}_{q,g}$$

where g runs over G and r state. This unitary transformation is different from the Bogoliubov-Tyablikov transformation (see (3-29)). They are different in types of the transformed operators as well as in purposes. (4-3) is a means for choosing an improved wave function

set through the transformed operators to give a better ground state energy. The method is to seek the values of the coefficients θ to minimize the energy. This will be discussed later. There should be similar expressions for $b_{p,r}$ and $b^{+}_{q,G}$. Accordingly, (4-3) can be generalized to become,

$$b_{p,f_1} = \sum_{g} \theta_p (g,f_1)\, b'_{p,f_1} \qquad (4\text{-}4)$$

$$b^{+}_{q,f_2} = \sum_{g} \theta^{*}_q (g,f_2)\, b^{+'}_{q,f_2}$$

In which f_1 and f_2 also run over G and r. It should be noted that θ and θ^{*} must satisfy the unitary and orthogonality conditions:

$$\sum_{f} \theta^{*}_p (g,f)\, \theta_p (g',f) = \delta_{gg'} \qquad (4\text{-}5)$$

Now, by substituting (4-4) into (4-2), the energy operator can be expressed as (4-6):

$$H = \sum_{\substack{f \\ h\ h'}} \langle f_1 | H_1 | f'_1 \rangle \left(\sum_{g_1} \theta^{*}_p (g_1,f_1)\, b^{+'}_{p,f_1}\right) \left(\sum_{g_2} \theta_p (g_2,f'_1)\, b'_{p,f'_1}\right)$$

$$+ \tfrac{1}{2} \sum_{\substack{p,q \\ f_1 f_2 \\ f'_1 f'_2}} \langle f_1 f_2 | V_{p,q} | f'_1\ f'_2 \rangle \left(\sum_{g_1} \theta^{*}_p (g_1,f_1)\, b^{+'}_{p,f_1}\right) \left(\sum_{g_2} \theta^{*}_q (g_2,f_2)\, b^{+'}_{q,f_2}\right) \left(\sum_{g'_1} \theta_p (g'_1\ f'_1)\, b'_{p,f'_1}\right) \left(\sum_{g'_2} \theta_q (g'_2\ f_2)\, b'_{g'_2,f'_2}\right)$$

(4-6)

Like f_1, the subscripts g_1, g_2, g'_1 and g'_2 must run over G and r.

By denoting,

$$\langle g_1 | A_p | g'_1 \rangle = \sum_{f_1\ f'_1} \langle f_1 | H_p | f'_1 \rangle\, \theta^{*}_p (g_1\ f_1)\, \theta_p (g'_1,f'_1)$$

$$\langle g_1\ g_2 | B_{pq} | g'_1\ g'_2 \rangle = \sum_{\substack{f_1\ f_2 \\ f'_1\ f'_2}} \langle f_1\ f_2 | V_{pq} | f'_1\ f'_2 \rangle\, \theta^{*}_p (g_1\ f_1)\, \theta^{*}_q (g_2\ f_2)\, \theta_p (g'_1\ f'_1)\, \theta_q (g'_2\ f'_2) \qquad (4\text{-}7)$$

(4-6) can be written as (4-8):

$$H = \sum_{\substack{p \\ g_1 g_1'}} \langle g_1 | A_p | g_1' \rangle \; b^{+\prime}_{p,g_1} \; b'_{p,g_1'}$$

$$+ \tfrac{1}{2} \sum_{\substack{p,q \\ g_1 g_2 \\ g_1' g_2'}} \langle g_1 g_2 | B_{pq} | g_1' g_2' \rangle \; b^{+\prime}_{p,g_1} \; b^{+\prime}_{q,g_2} \; b'_{p,g_1'} \; b'_{q,g_2'} \qquad (4\text{-}8)$$

In order to make an explicit derivation, G and r will now be inserted into (4-8) to yield (4-9):

$$H = \sum_{p} \langle G | A_p | G \rangle \; b^{+\prime}_{p,G} \; b'_{p,G} \qquad \text{(Term 1)}$$

$$+ \sum_{p} \langle G | A_p | r \rangle \; b^{+\prime}_{p,G} \; b'_{p,r} \qquad \text{(Term 2)}$$

$$+ \sum_{p} \langle r | A_p | G \rangle \; b^{+\prime}_{p,r} \; b'_{p,G} \qquad \text{(Term 3)}$$

$$+ \sum_{p} \langle r | A_p | r \rangle \; b^{+\prime}_{p,r} \; b'_{p,r} \qquad \text{(Term 4)}$$

$$+ \tfrac{1}{2} \sum_{p,q} \langle G\,G | B_{pq} | G\,G \rangle \; b^{+\prime}_{p,G} \; b^{+\prime}_{q,G} \; b'_{p,G} \; b'_{q,G} \qquad \text{(Term 5)}$$

$$+ \tfrac{1}{2} \sum_{p,q} \langle G\,G | B_{pq} | G\,r \rangle \; b^{+\prime}_{p,G} \; b^{+\prime}_{q,G} \; b'_{p,G} \; b'_{q,r} \qquad \text{(Term 6)}$$

$$+ \tfrac{1}{2} \sum_{p,q} \langle G\,G | B_{pq} | r\,G \rangle \; b^{+\prime}_{p,G} \; b^{+\prime}_{q,G} \; b'_{p,r} \; b'_{q,G} \qquad \text{(Term 7)}$$

$$+ \tfrac{1}{2} \sum_{p,q} \langle G\,r | B_{pq} | G\,G \rangle \; b^{+\prime}_{p,G} \; b^{+\prime}_{q,r} \; b'_{p,G} \; b'_{q,G} \qquad \text{(Term 8)}$$

$$+ \tfrac{1}{2} \sum_{p,q} \langle r\,G | B_{pq} | G\,G \rangle \; b^{+\prime}_{p,r} \; b^{+\prime}_{q,G} \; b'_{p,G} \; b'_{q,G} \qquad \text{(Term 9)}$$

$$+ \tfrac{1}{2} \sum_{p,q} \langle G\ r|B_{p,q}|G\ r\rangle\ b^{+'}_{p,G}\ b^{+'}_{q,r}\ b'_{p,G}\ b'_{q,r} \qquad \text{(Term 10)}$$

$$+ \tfrac{1}{2} \sum_{p,q} \langle G\ r|B_{p,q}|r\ G\rangle\ b^{+'}_{p,G}\ b^{+'}_{q,r}\ b'_{p,r}\ b'_{q,G} \qquad \text{(Term 11)}$$

$$+ \tfrac{1}{2} \sum_{p,q} \langle r\ G|B_{p,q}|G\ r\rangle\ b^{+'}_{p,r}\ b^{+'}_{q,G}\ b'_{p,G}\ b'_{q,r} \qquad \text{(Term 12)}$$

$$+ \tfrac{1}{2} \sum_{p,q} \langle r\ G|B_{p,q}|r\ G\rangle\ b^{+'}_{p,r}\ b^{+'}_{q,G}\ b'_{p,r}\ b'_{q,G} \qquad \text{(Term 13)}$$

$$+ \tfrac{1}{2} \sum_{p,q} \langle G\ G|B_{p,q}|r\ r\rangle\ b^{+'}_{p,G}\ b^{+'}_{q,G}\ b'_{p,r}\ b'_{q,r} \qquad \text{(Term 14)}$$

$$+ \tfrac{1}{2} \sum_{p,q} \langle r\ r|B_{p,q}|G\ G\rangle\ b^{+'}_{p,r}\ b^{+'}_{q,r}\ b'_{p,G}\ b'_{q,G} \qquad \text{(Term 15)}$$

$$+ \tfrac{1}{2} \sum_{p,q} \langle G\ r|B_{p,q}|r\ r\rangle\ b^{+'}_{p,G}\ b^{+'}_{q,r}\ b'_{p,r}\ b'_{q,r} \qquad \text{(Term 16)}$$

$$+ \tfrac{1}{2} \sum_{p,q} \langle r\ G|B_{p,q}|r\ r\rangle\ b^{+'}_{p,r}\ b^{+'}_{q,G}\ b'_{p,r}\ b'_{p,r} \qquad \text{(Term 17)}$$

$$+ \tfrac{1}{2} \sum_{p,q} \langle r\ r|B_{p,q}|G\ r\rangle\ b^{+'}_{p,r}\ b^{+'}_{q,r}\ b'_{p,G}\ b'_{q,r} \qquad \text{(Term 18)}$$

$$+ \tfrac{1}{2} \sum_{p,q} \langle r\ r|B_{p,q}|r\ G\rangle\ b^{+'}_{p,r}\ b^{+'}_{q,r}\ b'_{p,r}\ b'_{q,G} \qquad \text{(Term 19)}$$

$$+ \tfrac{1}{2} \sum_{p,q} \langle r\ r|B_{p,q}|r\ r\rangle\ b^{+'}_{p,r}\ b^{+'}_{q,r}\ b'_{p,r}\ b'_{q,r} \qquad \text{(Term 20)}$$

After combining terms (6) and (7), (8) and (9), (10) and (13), (11) and (12) respectively, the energy operator takes the form:

$$H = \sum_p \langle G|A_p|G\rangle b^{+'}_{p,G} b'_{p,G} + \tfrac{1}{2}\sum_{p,q} \langle G\,G|B_{p,q}|G\,G\rangle b^{+'}_{p,G} b^{+'}_{q,G} b'_{p,G} b'_{q,G}$$

$$+ \sum_p \langle G|A_p|r\rangle b^{+'}_{p,G} b'_{p,r} + \sum_{p,q} \langle G\,G|B_{p,q}|r\,G\rangle b^{+'}_{p,G} b^{+'}_{q,G} b'_{p,r} b'_{q,G}$$

$$+ \sum_p \langle r|A_p|G\rangle b^{+'}_{p,r} b'_{p,G} + \sum_{p,q} \langle r\,G|B_{p,q}|G\,G\rangle b^{+'}_{p,r} b^{+'}_{q,G} b'_{p,G} b'_{q,G}$$

$$+ \sum_p \langle r|A_p|r\rangle b^{+'}_{p,r} b'_{p,r} + \sum_{p,q} \langle r\,G|B_{p,q}|r\,G\rangle b^{+'}_{p,r} b^{+'}_{q,G} b'_{p,r} b'_{q,G}$$

$$+ \sum_{p,q} \langle G\,r|B_{p,q}|r\,G\rangle b^{+'}_{p,G} b^{+'}_{q,r} b'_{p,r} b'_{q,G}$$

$$+ \tfrac{1}{2}\sum_{p,q} \langle G\,G|B_{p,q}|r\,r\rangle b^{+'}_{p,G} b^{+'}_{q,G} b'_{p,r} b'_{q,r}$$

$$+ \tfrac{1}{2}\sum_{p,q} \langle r\,r|B_{p,q}|G\,G\rangle b^{+'}_{p,r} b^{+'}_{q,r} b'_{p,G} b'_{q,G}$$

$$+ \text{terms (16-20) in (5-9).} \qquad (4\text{-}10)$$

When Bogoliubov developed this approximate second quantization method, one of the main purposes was to find a lower energy eigenvalue, E'_G, instead of E_G, in (2-4). Because of $i = j = 1$, (2-4) is now re-expressed as (4-11).

$$E_g = M\,w^G + \tfrac{1}{2}\sum_{p,q} \langle G\,G|V_{p,q}|G\,G\rangle \qquad (4\text{-}11)$$

In other words, he wanted to determine the energy eigenvalues to be as low as possible by minimizing the functional,

$$\text{Min} \quad \frac{\Psi \cdot H\Psi}{\Psi \cdot \Psi} \qquad (4\text{-}12a)$$

and treat

$$\frac{\Psi^G \cdot H\,\Psi^G}{\Psi^G \cdot \Psi^G} = E_G \qquad (4\text{-}12b)$$

as a trial solution and Ψ^G in (4-12b) as a first approximation to the ground state of the system. In order to accomplish this purpose

he then considered taking the weakly excited states into account so that the ground state can be depressed by this admixture, and each new creation and annihilition operators, $b^{+'}$ and b', will have its components in the original b^{+} and b respectively. This has been done by introducing Bogoliubov's unitary transformation in (4-4). In the language of the second quantization representation, this means to change,

$$\Psi^{G} = |1_{1,G}, 0_{1,r}, 1, 0 \ldots\ldots 1_{p,G}, 0_{p,r} \ldots. >$$

in which

$$n_{p,G} = 1 \qquad (4\text{-}13)$$

$$n_{p,r} = 0$$

to $\Psi^{G'}$ in which $n_{p,f}$ (f = G or r) will no longer have a definite value but rather, in an average sense,

$$n_{p,G} \simeq 1 \qquad (4\text{-}14)$$

$$n_{p,r} \simeq 0 \qquad (4\text{-}15)$$

and

$$n_{p,G} + n_{p,r} = 1 \qquad (4\text{-}16)$$

One must now minimize the energy operator subject to the unitary and orthonormality condition in (4-5). This can be done by the method of Lagrangian multipliers.[28]

When a minimum (or maximum as well) of a function, f(x,y) is to be found with the constraint of some auxiliary equations such as g(x,y) = c (c is a constant); a solution can be set up by writing a function, Λ, defined as,

$$\Lambda = f(x,y) + \lambda\, g(x,y) \qquad (4\text{-}17)$$

The parameter λ is called a Lagrangian multiplier. A necessary condition for finding the minimum is (4-18):

$$\frac{\partial \Lambda}{\partial x} = \frac{\partial f}{\partial x} - \lambda \frac{\partial g}{\partial x} = o$$

$$\frac{\partial \Lambda}{\partial y} = \frac{\partial f}{\partial y} - \lambda \frac{\partial g}{\partial y} = o \qquad (4\text{-}18)$$

$$\frac{\partial \Lambda}{\partial \lambda} = c - g = o$$

(4-12b) is a good illustrative example in which the functional $\frac{\Psi^G \cdot H\Psi^G}{\Psi^G \Psi^G}$ is to be minimized subject to the orthonormality condition : $\Sigma \Psi^G \Psi^G = 1$. The resulting equation may be written as,

$$H \Psi^G = \lambda \Psi^G \qquad (4\text{-}19)$$

in which $\lambda = E_G = M w^G + \frac{1}{2} \Sigma_{p,q} < G\ G|V_{p,q}|G\ G >$. In other words, the eigenvalue E_G, is entered as a Lagrangian multiplier. In the present discussion (4-12a), instead of (4-12b) is to be minimized subject to the condition (4-5) so that (see Ref. 13, p.208 and Ref. 27):

$$< G|A_p|G > + \Sigma_q < G\ G|B_{p,q}|G\ G > = \lambda_p(G) = w'_G$$

$$< G|A_p|G > + \Sigma_q < G\ G|B_{p,q}|r\ G > = 0 \qquad (4\text{-}20)$$

$$< r|A_p|G > + \Sigma_q < r\ G|B_{p,q}|G\ G > = 0$$

$$< r|A_p|r > + \Sigma_q < r\ G|B_{p,q}|r\ G > = \lambda_p(r) = w^{r'} + D^{r'}$$

The definition of A_p and $B_{p,q}$ is seen in (4-7).

Also, it is seen that because of (4-14 and 15)

$$b^{+'}_{p,G}\, b'_{p,G} = n_{p,G} \qquad (4\text{-}21)$$

$$= 1 - n_{p,r}$$

so that,

$$\sum_p \langle G|A_p|G\rangle b^{+'}_{p,G} b'_{p,G} + \tfrac{1}{4} \sum_{p,q} \langle G\,G|B_{p,q}|G\,G\rangle b^{+'}_{p,G} b^{+'}_{q,G} b'_{p,G} b'_{q,G}$$

$$= \sum_p \langle G|A_p|G\rangle n_{p,G} + \tfrac{1}{2} \sum_{p,q} \langle G\,G|B_{p,q}|G\,G\rangle n_{p,G} n_{q,G}$$

$$= \sum_p \langle G|A_p|G\rangle (1-n_{p,r}) + \tfrac{1}{2} \sum_{p,q} \langle G\,G|B_{p,q}|G\,G\rangle (1-n_{p,r})(1-n_{q,r})$$

$$= \left(\sum_p \langle G|A_p|G\rangle + \tfrac{1}{2} \sum_{p,q} \langle G\,G|B_{p,q}|G\,G\rangle\right).1$$

$$- \sum_p \left(\langle G|A_p|G\rangle + \tfrac{1}{2} \sum_{p,q} \langle G\,G|B_{p,q}|G\,G\rangle\right) n_{p,r} \qquad (4\text{-}22)$$

(4-22) is obtained by assuming that $n_{p,r} . n_{p,r} \simeq 0$. It is a good assumption because of (4-14) and (4-15) and it is consistent with the fact that, in the system of low intensity illumination, most molecules are actually in the ground state. Because of this fact terms (16-20) are negligible.

Applying (4-22), (4-20) and neglecting terms (16-20), the energy operator is finally expressed as (4-23):

$$H = H'_o + H'_1 + H'_2 + H'_3$$

$$H'_o = \sum_p (w'_G + D'_G) = E'_G$$

$$H'_1 = \sum_p (\Delta w^{r'} + D^{r'}) \; b^{+'}_{p,r} b'_{p,r}$$

$$H'_2 = \sum_{p,q} \langle G\,r|B_{p,q}|r\,G\rangle b^{+'}_{p,G} b^{+'}_{q,r} b'_{p,r} b'_{q,G}$$

$$H'_3 = \tfrac{1}{2} \sum_{p,q} \langle G\,G|B_{p,q}|r\,r\rangle b^{+'}_{p,G} b^{+'}_{q,G} b'_{p,r} b'_{q,r}$$

$$+ \tfrac{1}{2} \sum_{p,q} \langle r\,r|B_{p,q}|G\,G\rangle b^{+'}_{p,r} b^{+'}_{q,r} b'_{p,G} b'_{q,G} \qquad (4\text{-}23)$$

in which

$$\lambda_p(r) - \lambda_p(G) = w^{r'} + D^r - w_G = \Delta w^{r'} + D^{r'}$$

$$b^{+'}_{p,r}\, b^{+'}_{q,G}\, b'_{p,r}\, b'_{q,G} = n_{p,r'}\, n_{q,G} = n_{p,r} = b^{+'}_{p,r}\, b'_{p,r}$$

By defining

$$B^{+'}_{p,r} = b^{+'}_{p,r}\, b'_{p,G} \qquad (4\text{-}24)$$

$$B'_{p,r} = b^{+'}_{p,G}\, b'_{p,r}$$

and using (4-14 and 4-15), $B^{+'}$ and B' can be assigned to have the boson property (see Sec. 3.2). The energy operator is expressed in terms of $B^{+'}$ and B' as,

$$H - H'_o = H'_1 + H'_2 + H'_3 \qquad (4\text{-}25)$$

with

$$H'_1 = (\Delta w^{r'} + D^r)\, B^{+'}_{p,r}\, B'_{p,r}$$

$$H'_2 = \sum_{f,q} L'_{p,q}\, B^{+'}_{p,r}\, B'_{p,r} \qquad (4\text{-}25a)$$

$$H'_3 = \tfrac{1}{2} \sum_{p,q} M'_{p,q}\, (B^{+'}_{p,r}\, B^{+'}_{p,r} + B'_{p,r}\, B'_{p,r})$$

in which

$$L'_{p,q} = \langle G\ r | B_{p,q} | r\ G \rangle \qquad (4\text{-}25b)$$

$$M'_{p,q} = \langle G\ G | B_{p,q} | r\ r \rangle = \langle r\ r | B_{p,q} | G\ G \rangle$$

It is now a straightforward matter to apply the Bogoliubov-Tyablikov transformation which has been shown in Sec. 3-4 (from Eq. (3-27) to 3-33)).

For the case of h = 1, the Tyablikov equations are (4-36) (see (3-34a)),

$$[\Delta w' + D' - E(k)]\, U' + L'_{p,q}(k)\, U(k) + M'_{p,q}(k)\, V'(k) = o \qquad (4\text{-}26)$$

$$[\Delta w' + D' - E(k)]\, V(k) + L'_{p,q}(k)\, V'(k) + M'_{p,q}(k)\, U'(k) = o$$

and the transformed energy operator as,

$$H' = E'_G - \sum_{k,i} E'_i V'_i V'_i + \sum_{k,i} E_i A^{+'}_{k,i} A'_{k,i} \qquad (4\text{-}27)$$

4.3 Inclusion of Bogoliubov's Unitary Transformation

As mentioned earlier, the derivation from (4-2) to (4-25) has not been carried out before in the application of this method to the exciton problem of molecular crystals. As a matter of fact, it seems that (4-25) is set up without the process of the Bogoliubov's unitary transformation of (4-3). In other words, the basis functions are the ordinary free molecule set as in Chapter 2 and the energy operator is set up from (3-26) and then the Bogoliubov-Tyablikov canonical transformation is applied as shown in Chapter 3. This can be discussed in two ways: firstly, in many previous treatments (see, for example, p.120 of Ref. 4), the relation

$$L_{p,q} = M_{p,q} \tag{4-28a}$$

$$\langle\langle G\ r|V_{p,q}|r\ G\rangle = \langle G\ G|V_{p,q}|r\ r\rangle \tag{4-28b}$$

is used following from the neglect of electron-exchange effect. However, if the Bogoliubov's unitary transformation is fully employed, then

$$L'_{p,q} = M'_{p,q} \tag{4-29a}$$

$$\langle G\ r|B_{p,q}|r\ G\rangle = \langle G\ G|B_{p,q}|r\ r\rangle \tag{4-29b}$$

may be established, not because of the neglect of electron-exchange but rather because of

$$\Theta^{*}_{p}(f_1,f_2) = \Theta_{q}(f_1,f_2) \tag{4-30}$$

This can be shown explicitly,

$$L'_{p,q} = \langle G\ r|B_{p,q}|r\ G\rangle$$

$$= \sum_{f_1,f_1',f_2,f_2'} \langle f_1 f_2\ V_{p,q}\ f_1', f_2'\rangle\ \theta_p^*(f_1 G)\theta_q^*(f_2 r)\theta_p(f_1' r)\theta_q(f_2' G)$$

$$= \langle G\ G|V|G\ G\rangle\theta_p^*(G,G)\theta_q^*(G,r)\theta_p(G,r)\theta_q(G,G)$$

$$+ \langle G\ G|V|G\ r\rangle\theta_p^*(G\ G)\theta_q^*(G,r)\theta_p(G,r)\theta_q(r,G)$$

$$+ \langle G\ G|V|r\ G\rangle\theta_p^*(G,G)\theta_q^*(G,r)\theta_p(r,r)\theta_q(G,G)$$

$$+ \langle G\ r|V|G\ G\rangle\theta_p^*(G,G)\theta_q^*(r,r)\theta_p(G,r)\theta_q(G,G)$$

$$+ \langle r\ G|V|G\ G\rangle\theta_p^*(r,G)\theta_q^*(G,r)\theta_p(G,r)\theta_q(G,G)$$

$$+ \langle G\ G|V|r\ r\rangle\theta_p^*(G,G)\theta_q^*(G,r)\theta_p(r,r)\theta_q(r,G)$$

$$+ \langle G\ r|V|G\ r\rangle\theta_p^*(G,G)\theta_q^*(r,r)\theta_p(G,r)\theta_q(r,G)$$

$$+ \langle G\ r|V|r\ G\rangle\theta_p^*(G,G)\theta_q^*(r,r)\theta_p(r,r)\theta_q(G,G)$$

$$+ \langle r\ G|V|G\ r\rangle\theta_p^*(r,G)\theta_q^*(G,r)\theta_p(G,r)\theta_q(r,G)$$

$$+ \langle r\ r|V|G\ G\rangle\theta_p^*(r,G)\theta_q^*(r,r)\theta_p(G,r)\theta_q(G,G)$$

$$+ \langle r\ G|V|r\ G\rangle\theta_p^*(r,G)\theta_q^*(G,r)\theta_p(r,r)\theta_q(G,G)$$

$$+ \langle G\ r|V|r\ r\rangle\theta_p^*(G,G)\theta_q^*(r,r)\theta_p(r,r)\theta_q(r,G)$$

$$+ \langle r\ G|V|r\ r\rangle\theta_p^*(r,G)\theta_q^*(G,r)\theta_p(r,r)\theta_q(r,G)$$

$$+ \langle r\ r|V|G\ r\rangle\theta_p^*(r,G)\theta_q^*(r,r)\theta_p(G,r)\theta_q(r,G)$$

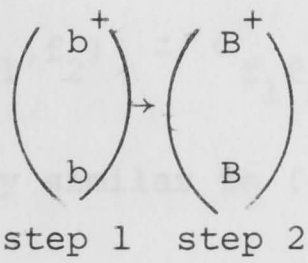
$$+ \langle r\ r|V|r\ G\rangle\theta_p^*(r,G)\theta_q^*(r,r)\theta_p(r,r)\theta_q(G,G)$$

$$+ \langle r\ r|V|r\ r\rangle\theta_p^*(r,G)\theta_q^*(r,r)\theta_p(r,r)\theta_q(r,G) \qquad (4\text{-}31)$$

$$
\begin{aligned}
M'_{p,q} &= \langle G\ G|B_{p,q}|r\ r\rangle \\
&+ \sum_{f_1,f_2,f_1',f_2'} \langle f_1 f_2|V_{p,q}|f_1',f_2'\rangle\ \Theta_p(f_1 G)\Theta_q^*(f_2 G)\Theta_p^*(f_1' r)\Theta_q(f_2' r) \\
&= \langle G\ G|V|G\ G\rangle\Theta_p^*(G,G)\Theta_q^*(G,G)\Theta_p(G,r)\Theta_q(G,r) \\
&+ \langle G\ G|V|G\ r\rangle\Theta_p^*(G,G)\Theta_q^*(G,G)\Theta_p(G,r)\Theta_q(r,r) \\
&+ \langle G\ G|V|r\ G\rangle\Theta_p^*(G,G)\Theta_q^*(G,G)\Theta_p(r,r)\Theta_q(G,r) \\
&+ \langle G\ r|V|G\ G\rangle\Theta_p^*(G,G)\Theta_q^*(r,G)\Theta_p(G,r)\Theta_q(G,r) \\
&+ \langle r\ G|V|G\ G\rangle\Theta_p^*(r,G)\Theta_q^*(G,G)\Theta_p(G,r)\Theta_q(G,r) \\
&+ \langle G\ G|V|r\ r\rangle\Theta_p^*(G,G)\Theta_q^*(G,G)\Theta_p(r,r)\Theta_q(r,r) \\
&+ \langle G\ r|V|G\ r\rangle\Theta_p^*(G,G)\Theta_q^*(r,G)\Theta_p(G,r)\Theta_q(r,r) \\
&+ \langle G\ r|V|r\ G\rangle\Theta_p^*(G,G)\Theta_q^*(r,G)\Theta_p(r,r)\Theta_q(G,r) \\
&+ \langle r\ G|V|G\ r\rangle\Theta_p^*(r,G)\Theta_q^*(G,G)\Theta_p(G,r)\Theta_q(r,r) \\
&+ \langle r\ r|V|G\ G\rangle\Theta_p^*(r,G)\Theta_q^*(r,G)\Theta_p(G,r)\Theta_q(G,r) \\
&+ \langle G\ r|V|r\ r\rangle\Theta_p^*(G,G)\Theta_q^*(r,G)\Theta_p(r,r)\Theta_q(r,r) \\
&+ \langle r\ G|V|r\ G\rangle\Theta_p^*(r,G)\Theta_q^*(G,G)\Theta_p(r,r)\Theta_q(G,r) \\
&+ \langle r\ G|V|r\ r\rangle\Theta_p^*(r,G)\Theta_q^*(G,G)\Theta_p(r,r)\Theta_q(r,r) \\
&+ \langle r\ r|V|G\ r\rangle\Theta_p^*(r,G)\Theta_q^*(r,G)\Theta_p(G,r)\Theta_q(r,r) \\
&+ \langle r\ r|V|r\ G\rangle\Theta_p^*(r,G)\Theta_q^*(r,G)\Theta_p(r,r)\Theta_q(G,r) \\
&+ \langle r\ r|V|r\ r\rangle\Theta_p^*(r,G)\Theta_q^*(r,G)\Theta_p(r,r)\Theta_q(r,r)
\end{aligned}
\tag{4-32}
$$

(4-31) is always equal to (4-32), i.e., (4-29) is established, as long as (4-30) holds true.

Secondly, in the previous treatments (see, for example, Ref. 4, p.121), the ways to formulate the matrix is via (see Eq. 3-12)):



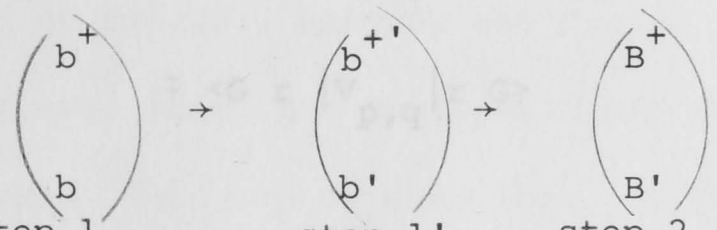
for example,

$$< G\ G|V|r\ r > \ b^{+}_{p,G}\ b^{+}_{q,G}\ b_{p,r}\ b_{q,r}$$

(4-33)

$$= < G\ G|V_{p,q}|r\ r > \ B_{p,r}\ B_{q,r}$$

However, if the Bogoliubov's unitary transformation in (4-3) is employed, then, the matrix element should be formulated as



and corresponding to (4-33)

$$< G\ G|V_{p,q}|r\ r > \ b^{+}_{p,G}\ b^{+}_{q,G}\ b_{p,r}\ b_{q,r}$$

$$= <f_1 f_2|V_{p,q}|f'_1 f'_2> \left(\sum_{f_1} \theta^{*}_{p}(f_1 G)\ b^{+'}_{p,f_1}\right)\left(\sum_{f_2} \theta^{*}_{q} f_2 G)\ b^{+'}_{q,f_2}\right)$$

$$\left(\sum_{f'_1} \theta_{p}(f'_1 r)\ b'_{p,f'_1}\right)\left(\sum_{f'_2} \theta_{q}(f'_2 r)\ b'_{q,f'_2}\right)$$

$$= \sum_{f_1 f_2 f'_1 f'_2} <f_1 f_2|V_{p,q}|f'_1 f'_2> \theta^{*}_{p}(f_1 G)\theta^{*}_{q}(f_2 G)\theta_{p}(f'_1 r)$$

$$\theta_{q}(f'_2 r) b^{+'}_{p,g}\ b^{+'}_{q,G}\ b'_{p,r}\ b'_{q,r}$$

$$= < G\ G|B_{p,q}|r\ r > B'_{p,r}\ B'_{q,r}$$

(4-34)

Perhaps, one might consider that the Bogoliubov's unitary transformation had been actually carried out in the process involving (4-28) and (4-33), but with one implicit condition that the Θ functions are nearly the delta function:

$$\Theta(f_1,f_2) \approx \delta_{f_1 f_2} \tag{4-35}$$

(4-35) is a condition very similar to (4-14 and 15), namely,

$$n_{p,G} \approx 1 \tag{4-14}$$

$$n_{p,r} \approx 0 \tag{4-15}$$

When (4-35) is substituted into (4-31), all terms in the right hand side are negligible except,

$$\langle G\ r|B_{p,q}|r\ G\rangle \approx \langle G\ r\ |V_{p,q}|r\ G\rangle\ \Theta^*_p(G,G)\Theta^*_q(r,r)\Theta_p(r,r)\Theta_q(G,G)$$

$$\approx \langle G\ r\ |V_{p,q}|r\ G\rangle \tag{4-36a}$$

accordingly,

$$L'_{p,q} \approx L_{p,q} \tag{4-36b}$$

In a similar way,

$$\langle G\ G|B_{p,q}|r\ r\rangle \approx \langle G\ G|V_{p,q}|r\ r\rangle \tag{4-37a}$$

$$M'_{p,q} \approx M_{p,q} \tag{4-37b}$$

because of (4-32) and (4-35), or alternatively, using (4-34):

$$B'_{p,r} = b^{+'}_{p,r}\ b'_{p,r}$$

$$= (\Theta^*_p(G,r)b^+_{p,G} + \Theta^*_p(r,r)b^+_{p,r})(\Theta_p(G,G)b_{p,G} + \Theta_p(r,G)b_{p,r})$$

$$\approx 0 + 0 + 0 + b^+_{p,r}\ b_{p,G}$$

$$\approx B_{p,r} \tag{4-38}$$

4.4 Ground-State Energy

From the derivation shown in Sec. 4.2, one can see that as far as (2-11) is concerned, (4-2) is its equivalent counterpart in the second quantization representation (cf. not the approximate second quantization method). If one does not want to follow Bogoliubov's method, the energy operator in (4-2) is always the starting point. It may be treated by Feynman diagrams, Green's function or other appropriate techniques which are beyond the scope of the present study. As long as (4-25), instead of (4-2) is used, it can be assured that the discussion is within the scheme of the approximate second quantization method. Moreover, one can see that in order to derive (4-25) from (4-2), several unique procedures such as (4-3) and (4-15) have to be introduced. Accordinly, the treatment developed by Bogoliubov, Tyablikov and Agranovitch is essentially different from that developed by Frenkel, Davydov and Craig.

Nevertheless, these two treatments are internally consistent among themselves. This can be seen that, on the one hand (4-25) is the energy operator for the exciton problem by the approximate second quantization method; the diagonalized energy operator is given in (4-27) in which the last term, i.e. $\sum_{k,i} E_i A^{+}_{k,i} A_{k,i}$, gives the excitation energy in terms of new pseudo-particle operators, A^{+} and A which have had both the Bogoliubov's unitary transformation and Bogoliubov-Tyablikov canonical transformation applied. The new operators do not diagonalize the total energy of a system that is excited but they do minimize the energy of the ground state. On the other hand, by the perturbation method, the energy operator must take the form as,

$$H = H_p + \tfrac{1}{2} \sum_{p,q} V_{p,q} \qquad (4\text{-}39)$$

with

$$I_{p,q} = \sum_{p,q} \langle \phi_p^r \phi_q \left| V_{p,q} \right| \phi_r \phi_q^r \rangle = \underline{R}_{p,q}^{-3} (\underline{M}^r)^2 \sum_{p,q} G_{p,q}^r \qquad (4\text{-}39a)$$

for the case of h = 1 in the co-ordinate representation. $\underline{M}^r$ had been defined in (2-21) and the factor G is called the dipole-dipole lattice sum (see Ref. 3, pp.54, 59). One of the advantages of this Frenkel-Davydov-Craig scheme is that[30,31] by expressing the energy operator as (4-39), it can concentrate primarily on the perturbation caused by the intermolecular interaction rather than on the solution of the many body problems or of the interaction between electron and electromagnetic field in the molecular crystal.

There is a difference of the ground state energy between these two treatments which can be seen in the final expressions of eigenvalues. In the perturbation method, it is known that E_G (see (2-4 and (2-14b)), the ground state energy, is used as a reference energy and the excitation spectrum is read off from this ground state energy. In other words, the crystal ground state is always the exciton vacuum state. It has been pointed by Craig,[25] that if the perturbation method ground state is corrected for van der Waals interaction, it too contains the second-order term, i.e. virtual excitation, and this correction amounts to the correction terms, i.e., $\sum_{ki} E_i |V_i|^2$ in the approximate second quantization method ground state. Of course, the correction term, $-\sum_{ki} E_{ki} |V_i|^2$, is small[7] as can be seen by the expression (3-13) and (3-14):

$$\begin{aligned} \langle 1 - N'' \rangle &= \langle N' \rangle \\ &= \langle B^+ B \rangle \qquad (4\text{-}40) \\ &= \langle \sum_{h,i} (U_{hi}^* A_{p,r}^+ + V_{hi} A_{p,r}) \sum_{h,i} (U_{hi} A_{p,r} + V_{hi}^* A_{p,r}^+) \rangle \end{aligned}$$

in which the notation, $\langle \quad \rangle$, means taking an average value over the whole lattice. Because of the assumptions that the average excitation is extremely small and the operators, A^+ and A, are those

of diagonalized ones, it follows that (see Ref. 11, p.113);

$$\begin{aligned} &< 1 - N'' > \simeq 0 \\ &< A^{+}_{p,r} A^{+}_{p,r} > = < A_{p,r}, A_{p,r} > = 0 \\ &< A^{+}_{p,r}, A_{p,r} > = N'_{p,r} \\ &< A_{p,r} A^{+}_{p,r} > = N^{+}_{p,r} + 1 \end{aligned} \tag{4-41}$$

and

$$< 1 - N'' > = \sum_{h,i} (|U_{hi}|^2 A^{+}_{p,r} A_{p,r} + |V_{hi}|^2 A_{p,r} A^{+}_{p,r})$$

$$= \sum_{h,i} |V_{hi}|^2 + \sum_{h,i} (|U_{h,i}|^2 + |V_{hi}|^2) N_{p,r}$$

for this quantity to be small and because of (3-23), the condition

$$\sum_{hi} |V_{hi}|^2 << 1 \tag{4-42}$$

must be satisfied. Consequently, $-\sum_{h,ki} E_i |V_{hi}|^2$ must be small compared with H_o and $\sum_{ki} E_i A^{+}_{k,i} A_{k,i}$.

Although the correction term, $-\sum_{k,i} E_i |V_{hi}|^2$, is small, it does contribute to the ground state energy because[11,14] of (3-26). It has been interpreted[15] as the zero-point exciton energy due to van der Waals interaction. In other words, the crystal ground state is not necessarily the exciton vacuum state because even in the ground state, there are some excitons as pointed out by Hopfield[6] and Anderson.[16] However, in view of the subscripts, k, in $-\sum_{k,i} E_i |V_i|^2$, this term affects all states to the same extent throughout and so does not vary any calculation of spectroscopic intervals such as the Davydov splittings. Probably because of this reason, in some treatments (see for example, Ref. 4, p.128), the excitation energy

of the molecular crystal in the approximate second quantization method is also read from the vacuum state so that,

$$H = H_o - \sum_{k,h,i} E_i |V_{h,i}|^2 + \sum_{k,i} Ei\, A^+_{k,i}\, A_{k,i} \tag{4-43}$$

$$H - H_o \simeq \sum_{k,i} E_i\, A^+_{k,i}\, A_{k,i}$$

CHAPTER 5

Second Comparison Between the Two Representations

5.1 Introduction

In the previous chapter, a theoretical comparison has been made between the co-ordinate representation and the occupation number representation. It is shown that, although the starting point for these two representations, i.e., (2-1) and (4-2) respectively, may be unitary equivalent, the results after derivation, i.e., (4-39) and (4-26) respectively, are not so related because the latter is derived within the scheme of the approximate second quantization method which is essentially different with the perturbation method. It would be of interest to see how much difference there would be numerically between these two representations.

The numerical comparison has been rarely done. When the theoretical formulation was discussed by Agranovitch[7] in 1959, a calculation[8] based on the approximate second quantization method was made on the second transition of crystalline anthrancene and comparing with that made by Craig and Hobbins.[2] Later a new calculation using an infinite chain of 3-level molecules as a model was attempted by Hoffmann,[10] comparing with that from a perturbation treatment. The results of these two comparisons are contrary to each other, in that the former was shown in considerable disagreement while the latter was claimed to be in good agreement. From then on, there is an increased interest in using the approximate second quantization method to deal with the exciton problem in molecular crystals. But all these treatments are devoted to theoretical discussion without actual evaluations.

Also, it is interesting to note that in any case (3-20), should be the starting point in principle, but in most cases replacement of (3-26) by (3-36) is taken for granted. In fact, in some discussions, Eq. (3-36) is considered as the equivalent counterpart of (2-17) and thus a one-to-one correspondence is assumed without dealing with the complexities shown in the previous chapter.

From the above discussion, one can see that not only are the actual calculations very scant, but also some of the theoretical formulation and the way to make a comparison between the two representations are rather confusing. The object of this chapter is to discuss and point out where these confusions have arisen.

5.2 Previous Work

The Davydov splitting can be found by solving the Tyablikov equation in (3-33). For the case of h = 2, the Tyablikov equation can be rearranged to become,

$$\begin{bmatrix} \Delta w+D+L_{11} - E & L_{12} & L_{12} & L_{12} \\ L_{11} & \Delta w+D+L_{11} + E & L_{12} & L_{12} \\ L_{21} & L_{21} & \Delta w+D+L_{22} - E & L_{21} \\ L_{21} & L_{21} & L_{21} & \Delta W+D+L_{22} + E \end{bmatrix} = 0 \qquad (5\text{-}1)$$

By denoting $w_{hi} = U_{hi} + V_{hi}$, one would then obtain,

$$\begin{bmatrix} (\Delta w+D+L_{11})^2 - E^2 & 2(\Delta w+D+L_{11})\, L_{12} \\ 2(\Delta w+D+L_{11})\, L_{21} & (\Delta w+D+L_{11})^2 - E^2 \end{bmatrix} = 0 \qquad (5\text{-}2)$$

After some arrangement, the eigenvalues can be found as,

$$E^2 = (\Delta w+D+L_{11})^2 \pm 2(\Delta w+D+L_{11})\, L_{12} \qquad (5\text{-}3)$$

with the Davydov splitting as,

$$\Delta E \simeq 2 L_{12} - a L_{12} \qquad (5\text{-}4)$$

in which $a = L_{12}/(\Delta w + D + L_{11})$.

For the second transition of crystalline anthracene, one can substitute the value of Craig and Hobbins into (5-4) to yield,

$$L_{12} = (2.3)^2 \quad 1382 = 7300 \text{ cm}^{-1}$$

$$\Delta w + D + L_{11} = 40000 \text{ cm}^{-1} \qquad (5\text{-}5)$$

$$\Delta E = 13300 \text{ cm}^{-1}$$

in which 2.3 is the transition moment and 1382 is the lattice sum for the inequivalent long axis interaction (see Ref. 2) the Davydov splitting is found as 13300 cm^{-1}. This value is different from that obtained from the perturbation method,[2] i.e., 14500 cm^{-1}, by more than one thousand reciprocal centimeters.

It is interesting to note that Agranovitch[8] did not use (5-3) directly. Instead he suggested using a procedure of "successive approximation" which consists of two steps. Step 1 is the case when H_3 term in (3-26) is discarded (see Eq. (3-35) to (3-40)) and step 2 is that when H_3 is included. This procedure is justified as[8] "when H_3 is absent, the Heitler-London approximation is used" and when it is included, the treatment is termed as that "without Heitler-London" approximation. In other words, the use of (3-26) or (3-35) as the exciton energy operator is explained as due to the difference of working with or without Heitler-London approximation. Let the superscripts "HL" and "WHL" denote with and without Heitler-London approximation. When i denots A_u band, the positive sign is used and B_u, minus sign. Following Agranovitch and Davydov:

Step 1 : (First approximation)

$$V_{hi}^{HL} = 0 \qquad (5\text{-}6a)$$

$$E_i^{HL} = \Delta w^r + D^r + L_{11} \pm L_{12} \qquad (5\text{-}6b)$$

so that

$$U_{hi}^{HL} \; (E^{HL} - (\Delta w + D)) = (L_{11} \pm L_{12}) \; U_{hi}^{HL} \qquad (5\text{-}6c)$$

Step 2 : (Next approximation)

$$V_{hi}^{WHL} \neq 0 \qquad (5\text{-}7a)$$

and from the Tyablikov equations,

$$(\Delta w^{r} + D^{r} - E_{i}^{WHL}) \; U_{hi}^{WHL} = (L_{11} \pm L_{12}) \; (U_{hi}^{WHL} + V_{hi}^{WHL}) \qquad (5\text{-}7b)$$

and the ratio:

$$V^{WHL} = \frac{\Delta w + D - E_{i}^{WHL}}{\Delta w + D + E_{i}^{WHL}} \; U^{WHL} \qquad (5\text{-}7c)$$

substituting (5-7c) and (5-6c) into (5-7b), one obtains,

$$[\,(\Delta w+D)^{2} - (E_{i}^{WHL})^{2}] = 2(\Delta w+D)\,[\,E_{i}^{HL} - (\Delta W^{r} + D^{r})] \qquad (5\text{-}8)$$

so that

$$E_{i}^{WHL} = (\Delta w+D)\,[\,2E^{HL} - (\Delta W^{r} + D^{r})] \qquad (5\text{-}9a)$$

and

$$U_{i}^{WHL} = \frac{(E_{i}^{HL} + \Delta W^{r} + D^{r})}{2\sqrt{E_{i}^{HL}\,(\Delta W^{r} + D^{r})}} \; U_{i}^{HL} \qquad (5\text{-}9b)$$

The Tyablikov equations are not used directly at all.

When (5-9a) is used for calculation, the Davydov splitting can be found from step 2, by substituting Craig and Hobbins's value as Step 1, to be $\simeq$ 13700 cm^{-1}. It is interesting to note that Agranovitch did not calculate in this way: instead he assumed that the experimental value "agrees" with E^{WHL}. Using formula (5-9a), he calculated back to get E^{HL} as $37.x10^{3}$ and $55.1x10^{3} cm^{-1}$ with the

splitting value as 18000 cm^{-1}. He then considered this value as that of Heitler-London approximation in the occupation number representation and compared with that of Craig and Hobbins as in the co-ordinate representation. A considerable disagreement is thus found.

Hoffmann[10] explained this disagreement as invalidated due to Agranovitch's improper use of $V_{hi} = 0$ and Eq. (5-9). He seemed to suggest that by using the Tyablikov equation directly, the results should be in good agreement. This is not the case as can be seen from (5-5). Moreover, Hoffmann's good agreement is applied in the case of one-molecule per unit cell and two-excited states while the present disagreement is that of two-per-cell and one excited state only. The two cases are quite different. In this connection, one can see that the previous claim, i.e. the results of two calculations are contrary to each other, is no longer true as their results apply to different cases. In view of the present interest, Hoffmann's result will be excluded hereafter and only the Agranovitch's calculation will be discussed.

5.3 Heitler-London Approximation

The remaining task is to discuss the numerical difference between the approximate second quantization method and the perturbation method. The difference is quite substantial as far as the second transition of crystalline anthracene is concerned. At first, it might be interesting to explain that in the next approximation procedure, why the Davydov splitting should be calculated backward from formula (5-9). This way of calculation may only be valid when it is assured that E^{WHL} in (5-9) is the observed energy. In view of the present discussion, it would be more logical to use Craig and Hobbins's value as E^{HL} and calculate forward to get E^{WHL}, because by following Agranovitch's reasoning, when H_3 in (3-26) is dropped, the energy operator becomes (3-35) which is described as the Heitler-London approximation in the occupation number representation, while (2-17) is called the Heitler-London approximation in the co-ordinate representation. Those two representations must be equivalent as far as the Heitler-London approximation is concerned. Using Craig and Hobbins's value in (5-9) to get E^{WHL}, one would obtain 13700cm^{-1}. The comparison of those calculated and observed can be shown in Table 1.

Table 1. Comparison of Davydov Splittings of 2500Å band of Crystalline Anthracene

Method \ Value		Davydov Splitting (cm^{-1})
Observed		14500[a]
Perturbation method		14600[b]
ASQ method	using H-L approx.	13000[c] (18000)
	using "next" approx.	13700[d]
	using Tyablibov Eq.	13300

a. Ref. 22. b. Ref. 2.

c. Although 18000 cm^{-1} was what Agranovitch obtained, he used different observed value. For comparison, the value from Ref. 22 is used here and calculated back, following Agranovitch's method, to get E^{WHL} from (5-9).

d. Value from Ref. 2 is used as E^{HL} to calculate forward to get E^{WHL} from (5-10a).

It is true that with this new procedure, the disagreement still exists, but, at least, it is more consistent. As can be seen from Table I, the disagreement becomes less pronounced.

Perhaps, Agranovitch's Heitler-London approximation has different meanings in different treatments. In other words, he might refer to the treatment in (2-17) as the Heitler-London approximation in the perturbation method, while that of (3-35) is from the approximate second quantization method. This can be supported by the following argument : it is true that the Frenkel-Davydov Craig exciton approach to molecular crystals can be called[18,19,20] a Heitler-London approximation because the exciton in molecular crystal is considered in a manner analogous to the Heitler and London theory of diatomic systems. But by taking two excitons such as,

$$\phi_p^r \, \phi_q^r \, \pi_s \, \phi_s^G = \phi^G \ldots \phi_p^r \ldots \phi_q^r \ldots \phi_N \qquad (5\text{-}10)$$

or more, into account, the treatment should be analogous to the inclusion of ionic character as, in the case[21] of hydrogen molecule:

$$\Phi = (\phi_1^a \, \phi_2^b + \phi_2^a \, \phi_1^b) + \varepsilon \, (\phi_1^a \, \phi_2^a + \phi_1^b \, \phi_2^b) \qquad (5\text{-}11)$$

in which ϕ is the hydrogenic wave function, and the first term is the atomic and the second, the ionic term. In other words, the double-excitations in (5-10) are taken as analogous to the ionic term in (5-11) so that, in the co-ordinate representation, the wave function of a molecular crystal with the double excitation term included, takes the form,[18]

$$\Psi_G' = \Psi_o + \varepsilon \, \Psi_{II} \qquad (5\text{-}12)$$

in which

$$\varepsilon << 1$$

$$\Psi_o = \sqrt{\frac{1}{N}}\ \pi_p \phi_p^G$$

$$\Psi_{II} = \sqrt{\frac{1}{N(N-1)}}\ \sum_{p,q} \exp[i(\underline{K}.\underline{R}_p + \underline{k}.\underline{R}_q)]\phi_p^r\ \phi_q^r \prod_{\substack{s \\ (\neq p) \\ (\neq q)}} \phi_s^G$$

It is important to note that the variation parameter, ε, would be present no matter which representation is being used. In the case of hydrogen molecule, its presence seems more logical than that of the molecular orbital method in which $\varepsilon = 1$, and thus there would be as much ionic character as covalent. In the case of molecular crystal, its presence seems consistent with the fact that, in conditions of low intensity of radiation, two-exciton terms such as (5-11) are negligible. Perhaps, one might suspect that it should be acceptable, if the energy operator in (3-26) is of a perturbation type such as,

$$H = H_1 + H_2 + H_3 \qquad (5\text{-}13)$$

in which

$$H_2 \tilde{} \varepsilon\ H_1$$

$$H_3 \tilde{} \varepsilon\ H_2$$

regardless of which representation is being used as long as the variation parameter exists, implicitly or explicitly. However, in view of the Tyablikov equation in (5-1), where there is M (= L) rather than H_3 ($\tilde{}\varepsilon\ H_2$) present, one can see that there is not any variation parameter existing. It seems that, unless the meaning of the Heitler-London approximation used by Agranovitch, Davydov is different with that used by Heller,[18] Dexter[19] and others,[20] the so-called "without Heitler-London" approximation is somewhat mis-leading.

In other words, in the Frenkel-Davydov-Craig method, the treatment can also be improved by dropping the Heitler-London restriction as shown in (5-12) and when this is done, the secular equation is certainly not that of Tyablikov-type, but perhaps, takes on a form and that H_3 can be discarded plausibly and the eigenvalues can be found as that of (3-17).

From the above discussion, one can now go back to reconsider the meaning of the two-exciton terms. Since the derivation in Sec. 4.2 includes only the G- and r-th states and does not include any others such as the s-th or 2r-th (double excitations) states, one should recognize that the meaning of the so-called two-exciton terms is not that of (5-12) in which the Heitler-London restriction is dropped. Perhaps, B^+B^+ and B B could be termed as "virtual" or "internal" two-exciton terms in contrast to the real excitons produced by the external radiation. In principle, there should be three- or four-(virtual) exciton terms from (4-2) within the accuracy of two-particle interaction, but they are neglected due to (4-14). It should be pointed out that the real two-exciton such as (5-10) had also been dropped during the derivation of the energy operator from the procedure of (4-4) in which,

$$b_{p,f} = \sum_g \Theta_p(g,f) b'_{p,r} \qquad (5\text{-}14)$$

g runs over G and r-th state only.

As for the next approximation, one immediate question is that why it is proposed and used for evaluation instead of using the Tyablikov equation? Does this mean the Tyablikov equation is incorrect? Certainly this could not be the case as it has been used successfully in the antiferromagnetism calculation. In fact, it is an integral part of the approximate second quantization method developed by Bogoliubov. Since Agranovitch and Davydov did not give

an explanation, the real intention of the next approximation can only be guessed here as they recognized implicitly that there are Θ functions appearing in L and M. The first approximation refers to the case in which M is dropped so that $V_{hi} = 0$ and the next approximation is that in which M is reintroduced as a correction. If so, because of (4-29), M can not be dropped at all. Accordingly, (5-7b) can not be substituted by (5-6c) to yield (5-8). In fact, from (4-29) and from the argument discussed above, there should be no such "Heitler-London" or first approximation in the approximation second quantization method unless, perhaps, an artificial condition is imposed which limits the derivation to the single excitation only.

Also, from (5-9), the Davydov splitting in the next approximation may be expressed as,

$$\Delta E \simeq 2L_{12} - \frac{L_{11}}{\Delta w + D} L_{12} \qquad (5\text{-}15)$$

Comparing (5-15) with (5-4), one can see that there is no definite relationship between $\frac{L_{11}}{\Delta w + D}$ and $\frac{L_{12}}{\Delta w+D+L_{11}}$. In other words, there is no theoretical proof that the ratio of $\frac{L_{11}}{\Delta w+D}$ will always be equivalent to that of $\frac{L_{12}}{\Delta w+D+L_{11}}$. Therefore, the numerical results of the next approximation do not truly represent that of the Tyablikov equation. The Tyablikov equation should be employed in any case.

Up to the present, only the 2500Å band of crystalline anthracene has been chosen for discussion. For this intense system, there is no need[1,2] for a correction for coupling with other band systems. If the 3800 Å band system is chosen, other effects such as band-to-band coupling should be taken into account as well as electron-exchange and charge-transfer effects,[23] then the situation is too complicated to draw any useful conclusion such as[8] "for a weak transition, the difference between E^{WHL} and E^{HL} is not large".

Although it is true that if one works on a hypothetic band, without the intensity-stealing process, with band position and transition moment as that of 3800Å, the calculated Davydov splitting between (5-4) and (2-17) are found to have only a small difference because[1] of a $\sim \frac{1}{600}$.

The difference of calculated Davydov splitting between the perturbation method and the approximate second quantization method for the various combination of the transition moment, band position and dipole-dipole interaction sum can be shown from Figs. 1 to 4. In Fig. 1, the difference in terms of wave number (cm^{-1}) is plotted against the dipole-dipole interaction ($cm^{-1}\ A^{-2}$) while in Figs. 2,3 and 4, the difference in terms of percentage ($\simeq {}^{a}/\Delta E$) is plotted against the dipole-dipole interaction sum, the transition moment and the band position respectively. From those figures, one can see that the difference of calculated Davydov splitting between the two treatments can be great only when the transition moment is strong, i.e. M > 2.0Å; perhaps, this is one of the reasons that the approximate second quantization treatment can only be applied to the weakly excited and ground states. When the transition moment is weak (M<2.0Å) or the dipole-dipole interaction is small ($G < 1000\ cm^{-1}A^{-2}$), the difference of calculated Davydov splitting is rather small. It might be satisfying to state that the perturbation method and the approximate second quantization method are different both theoretically and numerically. Moreover, the former method is in the co-ordinate representation while the latter is in the occupation number representation and there is no unitary equivalent relationship between them. In some cases, the numerical differences are minor while in others, great. The use of either approach is to be decided by comparing with the experimental value and by recoursing to the particular problem studied.

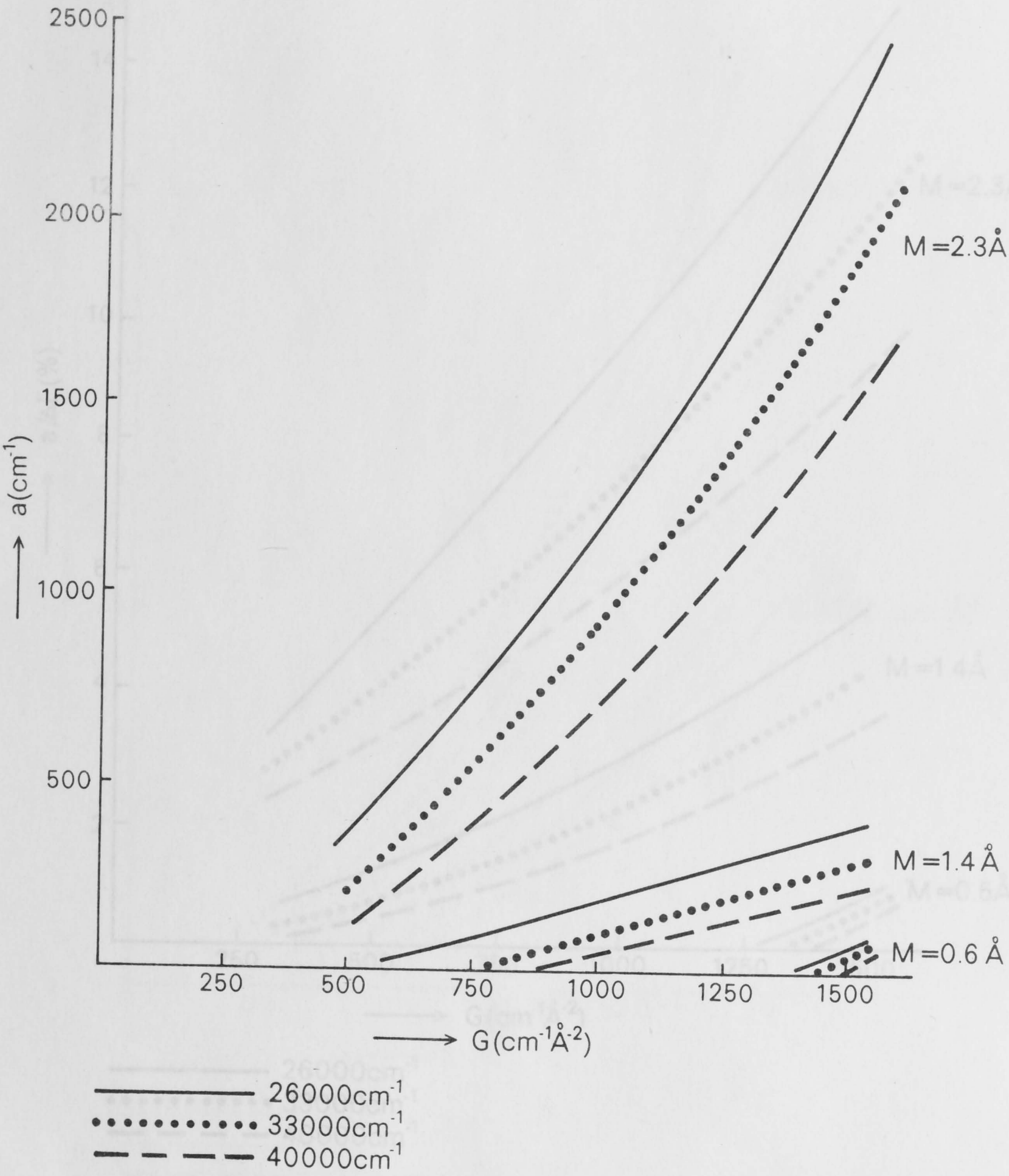


Fig. 1 Relation between difference in Davydov Splitting and dipole-dipole interaction sum for various band position and transition moment.

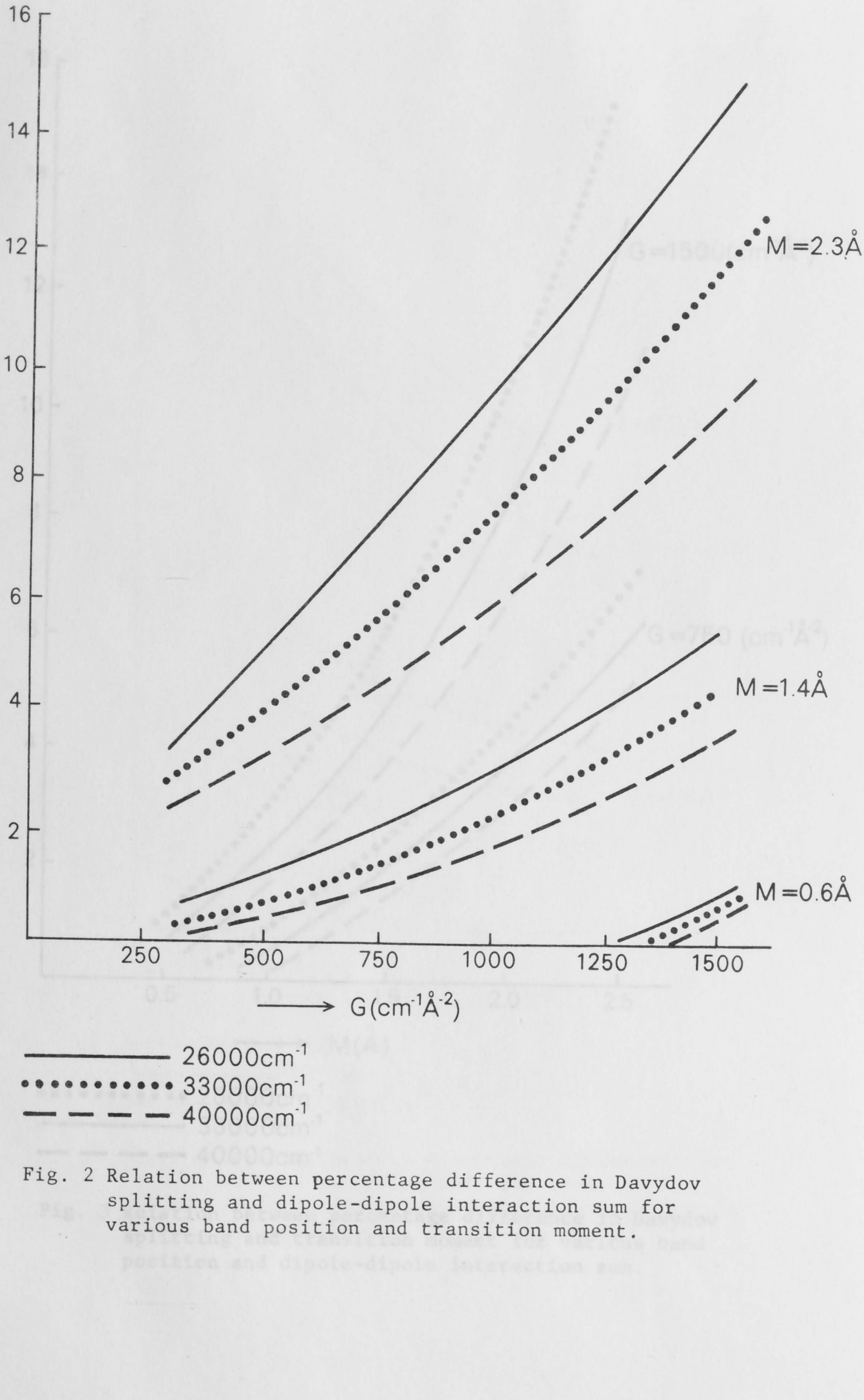


Fig. 2 Relation between percentage difference in Davydov splitting and dipole-dipole interaction sum for various band position and transition moment.

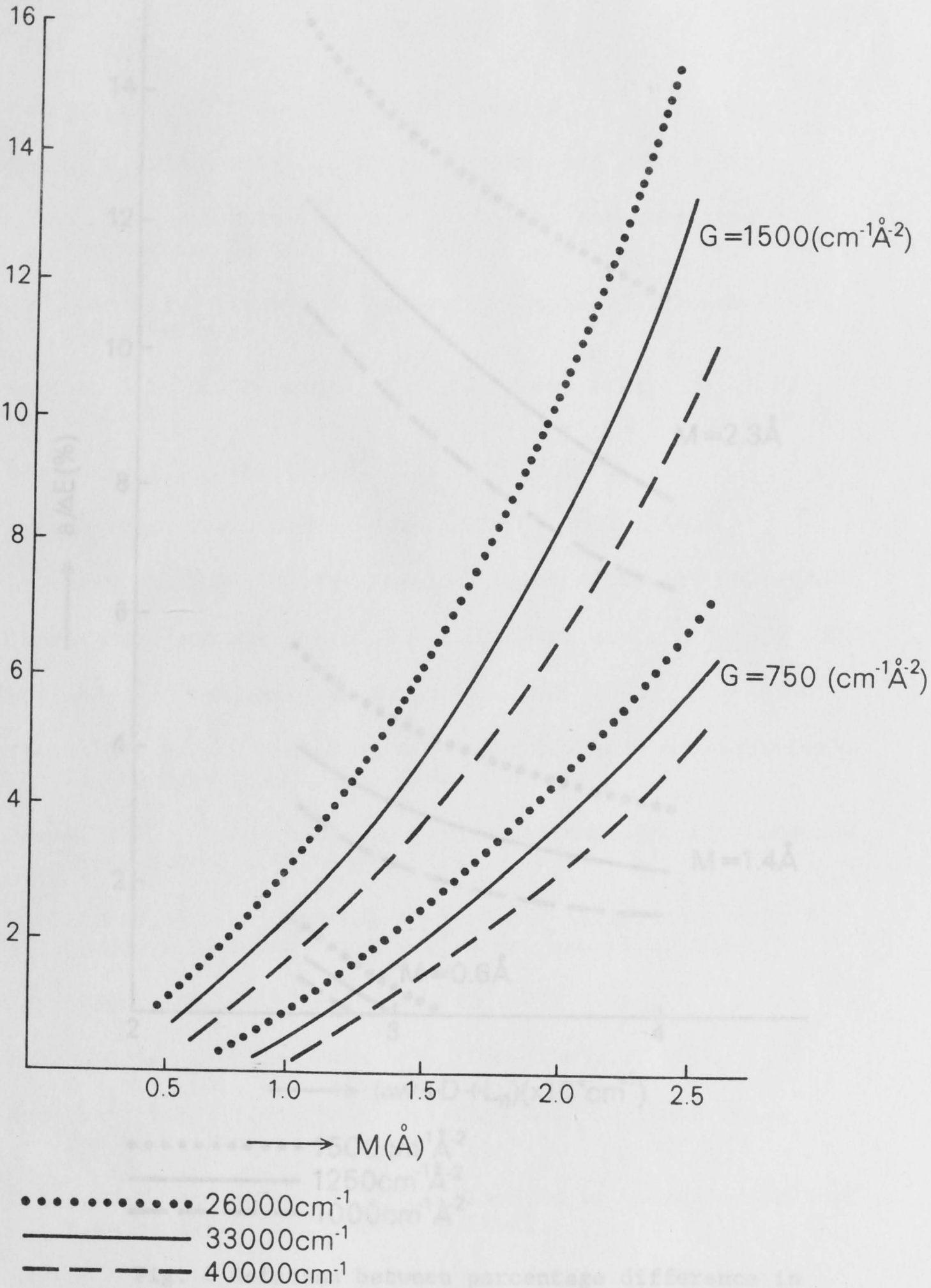


Fig. 3 Relation between percentage difference in Davydov splitting and transition moment for various band position and dipole-dipole interaction sum.

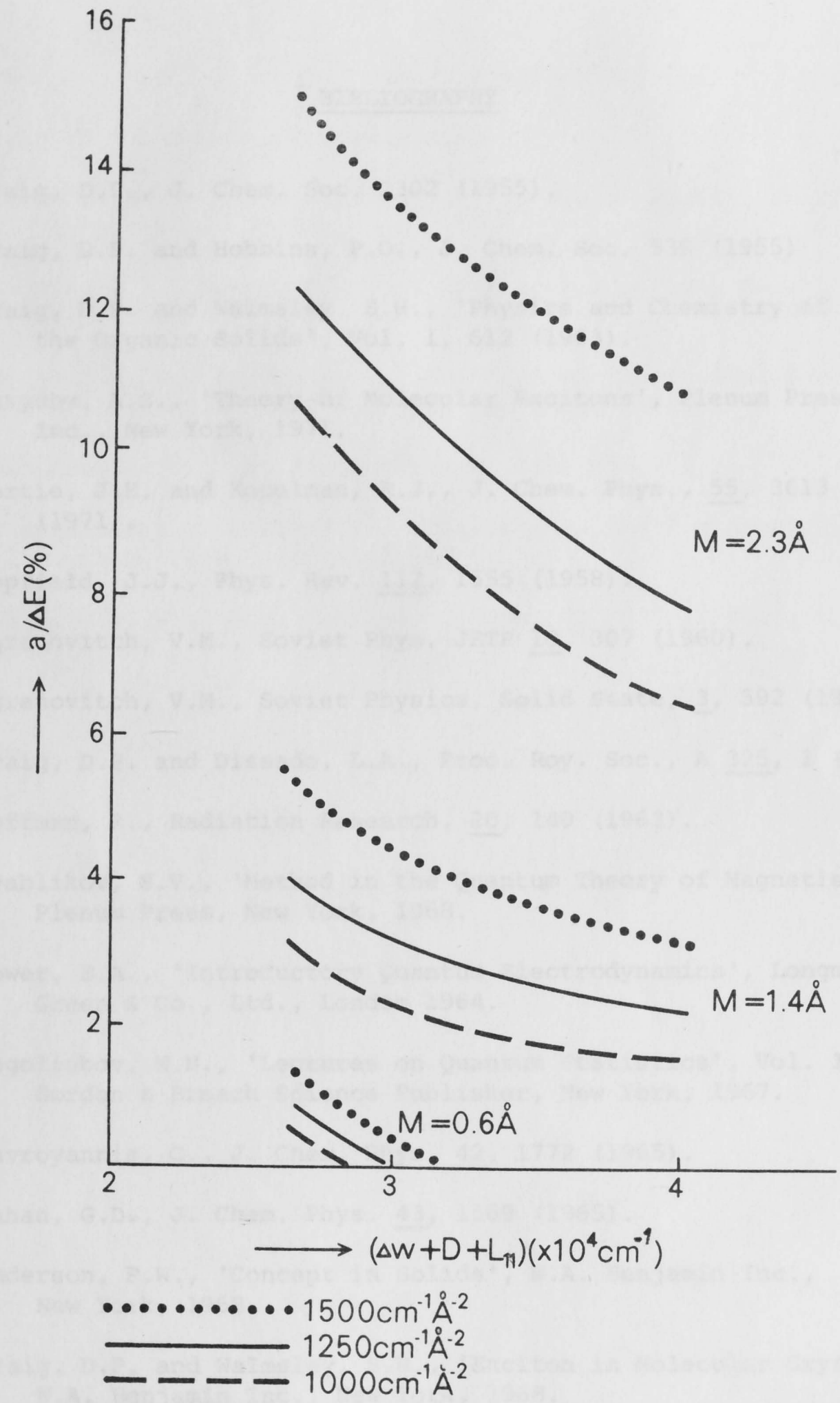


Fig. 4 Relation between percentage difference in Davydov splitting and band position for various transition moment and dipole-dipole interaction sum.

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